PB 168 865

ENVIRONMENTAL HEALTH SERIES
Air Pollution

METHODS OF MEASURING AND MONITORING ATMOSPHERIC SULFUR DIOXIDE

3.00 0.75 56 BAC

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service

METHODS OF MEASURING AND MONITORING ATMOSPHERIC SULFUR DIOXIDE

Seymour Hochheiser
Robert A. Taft Sanitary Engineering Center

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Division of Air Pollution

Cincinnati, Ohio

August 1964

The **ENVIRONMENTAL HEALTH SERIES** of reports was established to report the results of scientific and engineering studies of man's environment: The community, whether urban, suburban, or rural, where he lives, works, and plays; the air, water, and earth he uses and re-uses; and the wastes he produces and must dispose of in a way that preserves these natural resources. This **SERIES** of reports provides for professional users a central source of information on the intramural research activities of Divisions and Centers within the Public Health Service, and on their cooperative activities with State and local agencies, research institutions, and industrial organizations. The general subject area of each report is indicated by the two letters that appear in the publication number; the indicators are

AP - Air Pollution
AH - Arctic Health
EE - Environmental Engineering
FP - Food Protection
OH - Occupational Health
RH - Radiological Health
WP - Water Supply and Pollution Control

Triplicate tear-out abstract cards are provided with reports in the **SERIES** to facilitate information retrieval. Space is provided on the cards for the user's accession number and additional key words.

Reports in the **SERIES** will be distributed to requesters, as supplies permit. Requests should be directed to the Division identified on the title page or to the Publications Office, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio 45226.

Public Health Service Publication No. 999-AP-6

FOREWORD

Use of uniform analytical procedures for the determination of air pollutants would eliminate many of the difficulties presently encountered in the evaluation of data produced by the various analysts in the field of air pollution control. It is very difficult to assess and compare the nature and amount of air pollutants present in different environments when many and various methods are employed, each subject to different interferences and to inherent and systematic errors. So that the data reported may be more meaningfully utilized by people engaged in the various aspects of air pollution, it is desirable to have uniform operating procedures.

A literature review of methodology relating to the measurement of atmospheric sulfur dioxide and a description of recommended methods are presented in this report.

Selection of the methods described in detail herein for manual and automatic sampling and analysis of atmospheric sulfur dioxide was based on information currently available. It is recognized that further information on the methodology is desirable. It is also recognized that new, more nearly ideal methods may be developed. Further research and investigation to those ends is to be desired.

This publication of the Division of Air Pollution, Public Health Service, is intended to serve as a resource document for those involved in measurement of pollution and in research on new or improved methods, and for those who seek to bring about widespread agreement in matters concerning measurement of pollution.

Vernon G. MacKenzie
Chief, Division of Air Pollution
Bureau of State Services
Public Health Service
U. S. Department of Health,
Education, and Welfare

ACKNOWLEDGEMENTS

Grateful appreciation is extended to those individuals who gave unselfishly of their time and effort in reviewing this report and in contributing many helpful suggestions. The author wishes to acknowledge particularly the assistance and support provided by: Members of the Interbranch Chemical Advisory Committee, Division of Air Pollution; by Dr. Aubrey P. Altshuller, Gilbert L. Contner, Thomas R. Hauser, Charles L. Punte, Jr., Dr. Bernard E. Saltzman, Stanley F. Sleva, Mario Storlazzi, Elbert C. Tabor; and by Austin N. Heller and Jean J. Schueneman, Technical Assistance Branch, Division of Air Pollution; and by John S. Nader, Laboratory of Engineering and Physical Sciences, Division of Air Pollution.

CONTENTS

ABSTRACT vii
CRITERIA FOR SELECTION OF RECOMMENDED METHODS 1
Manual Sampling and Analysis 1
Sensitivity 1
Specificity 1
Reproducibility 1
Stability of Reagents and Products 2
Collection Efficiency 2
Simplicity and Directness 2
Difficulty in Calibration 3
Automatic Instrumental Methods 3
Speed of Reaction 3
Temperature Coefficient 3
Instrument Drift 4
Flow or Pressure Regulation 4
Instrument Maintenance Requirement 4
RECOMMENDED METHODS 4
Recommended Methods for Manual Sampling and Analysis 4
West and Gaeke Method 4
Introduction 4
Reagents 5
Apparatus 6
Analytical Procedure 6
Preparation of Calibration Curve 8
Discussion of Procedure 8
Hydrogen Peroxide Method 9
Introduction 9
Reagents 9
Apparatus 10
Analytical Procedure 10
Discussion of Procedure 11
Recommended Procedure and Specifications for Automatic Monitoring Instrument 12
Electroconductivity Analyzer 12
Introduction 12
Reagents 12
Apparatus 13
Calibration 14
Procedure 15
Instrument Performance Specifications 16
Discussion 17

COMPARISON OF METHODS CONSIDERED 18
Manual Methods 18
Instrumental Methods 23
MANUAL METHODS CONSIDERED IN ADDITION TO RECOMMENDED METHODS 23
Colorimetric Methods 23
Fuchsin-Formaldehyde Method 23
Stratman Method 26
Barium Chloranilate Method 26
Zinc Nitroprusside Method 26
Astrazone Pink Method 27
Diazo Dye Method 27
Thorium Borate-Amaranth Dye Method 28
Indirect Ultraviolet Determination of SO_2 by Means of Plumbous Ion 28
Ferrous-Phenanthroline Method 29
Polarographic Method 29
Iodimetric Methods 30
Iodine Method 30
Direct Iodine Method 30
Iodine-Thiosulfate Method 31
Turbidimetric Method 31
Cumulative Methods 32
Lead Peroxide Candle Method 32
Test Paper Method 34
Detector Tubes 35
INSTRUMENTAL METHODS CONSIDERED IN ADDITION TO RECOMMENDED METHODS 35
Potentiometric Methods 35
Photometric Methods 37
Analyzer "A" 37
Analyzer "B" 38
Analyzer "C" 39
Analyzer "D" 40
Air Ionization Method 41
REFERENCES 43

ABSTRACT

A literature review of methodology relating to the measurement of atmospheric sulfur dioxide, a detailed description of recommended methods, and criteria for selection of recommended methods are presented in this report. This publication is intended to serve as a resource document for those involved in measurement of pollution and in research on new or improved methods, and for those who seek to bring about widespread agreement in matters concerning measurement of pollution.

CRITERIA FOR SELECTION OF RECOMMENDED METHODS

Manual Sampling and Analysis

Evaluation of methods for the measurement of air pollutants was based upon an examination of systematic characteristics such as: Sensitivity, specificity, reproducibility, stability of reagents and products, collection efficiency, simplicity and directness, and difficulty of calibration.

SENSITIVITY

The quantity of air needed to be sampled to provide a detectable amount of the air pollutant is a function of the sensitivity of the analytical technique. To measure fluctuation in pollution amounts during short-term fumigations it is necessary to use methods capable of detecting extremely small quantities of the gaseous pollutant. When integrated values over a longer time interval are desired a less sensitive method is applicable. Nevertheless, methods capable of sensing short-term fluctuations in gas concentrations produce more meaningful data, and a highly sensitive method is, therefore, most often desirable.

SPECIFICITY

The effect of interfering materials present in the concentration range anticipated is an important consideration in the selection of suitable air-monitoring methods. In many instances it is possible to eliminate interfering materials by selective absorption or by other chemical reactions and thus avoid errors in analysis. At times it may be desirable to monitor with a nonspecific method that measures a group of compounds that have similar chemical properties and produce the same physiological response. A knowledge of individual components is, however, extremely valuable in interpretation of the data.

REPRODUCIBILITY

Reproducibility is a measure of the reliability and stability of the equipment, reagents, and technique employed in the method. The accuracy of the method can be no better than its reproducibility. Relatively good reproducibility does not, however, necessarily indicate relatively high accuracy. Accuracy, which is a measure of the deviation from a true value, is determined by measuring known amounts of a material and observing the correspondence between the measured and the true values. In air analysis wherein many

methods rely upon the removal of the pollutant from the air mass, accuracy is a function of collection or separation efficiency, flow metering, analytical variation, and other sources of error.

STABILITY OF REAGENTS AND PRODUCTS

Reagents and absorbents that have comparatively long shelf lives are advantageous. Their use eliminates the need for frequent reagent preparation and calibration. Absorbents that are easily susceptible to changes in composition and reactivity owing to light, temperature, turbulence, or air oxidation may produce serious errors in the analysis. If reaction products formed in air sampling are unstable, the method becomes unsuitable for use when there is a time lag between sampling and analysis, and the method cannot, therefore, be employed in certain automatic sampling equipment such as sequential samplers, though it may be satisfactory for automatic, continuous analyzers.

COLLECTION EFFICIENCY

The collection efficiency of methods that require scrubbers for the collection of a gaseous impurity depends upon the chemical nature of the absorbent and the pollutant, the physical condition during gas-liquid contact, and the sampling rate, which in effect controls the time of contact between the phases. The latter condition is particularly applicable to the physical retention techniques used in adsorption processes. Methods selected for aerosol collection depend largely upon the size of the particulates in the air or gas stream. To avoid using multiple separators in a sampling system, a collection efficiency of greater than 95 percent is generally required of one collector. It would, however, be permissible to use a sampling system having a relatively low collection efficiency provided that the desired sensitivity, reproducibility, and accuracy are obtainable. One method of determining collection efficiency is to connect similar collectors in series downstream and measure the ratio of pollutant occurring in the second and third units to that in the upstream unit. This is not an absolute method of determining efficiency since there may be a systematic threshold concentration below which no reaction occurs. Collection efficiency is determined by introducing known amounts of gas or aerosol at different dilutions. A method that has been previously calibrated and results in relatively high collection efficiency may be used as a standard for comparison of another method provided that the methods are both subject to the same interferences.

SIMPLICITY AND DIRECTNESS

When a simple technique gives the same degree of accuracy as a more complicated and time-consuming method, one would obviously choose the simpler technique, except, perhaps, when equipment costs render prohibitive the use of the simpler method.

Indirect methods are subject to greater inaccuracies owing to calibration difficulties and should be avoided whenever possible. Factors that influence simplicity are the number and difficulty of unit operations and the type of laboratory and field sampling controls required.

DIFFICULTY IN CALIBRATION

An ideal method would be one in which a specific compound of known composition is formed that is not subject to temperature, light sensitivity, or other instabilities and that can be measured directly and without interference from other compounds. In this event the quantity of product formed is directly related to the concentration of the reactants if a quantitative reaction is assumed. To determine the efficiency of reaction, a known quantity of the pollutant is introduced into the system at various concentrations corresponding to those existing in ambient air, and the amount recovered is determined. The techniques available for this type of standardization are dynamic dilution and static dilution. The effect of interferences can also be determined by similar techniques. After primary calibration of the system in the manner indicated above, secondary calibration methods can be employed, that is, standard solutions, conductivity cells of known resistance, and so forth.

Automatic Instrumental Methods

All the factors pertinent to the manual measurement of pollutants apply to measurement in continuous, automatic recording instruments. Other important parameters are: Speed of reaction, temperature coefficient, instrument drift, flow or pressure regulation, and instrument maintenance requirement.

SPEED OF REACTION

The time required to attain reaction equilibrium is an important consideration in the choice of reagent to be used in continuous analyzers, particularly in colorimetric recorders. Many colorimetric methods require a definite time for complete reaction, and it may become necessary, therefore, to alter reagent composition or calibrate at a definite time after sampling prior to complete reaction, to attain conditions consistent with instrument response. Instrument response, which is a function of flow rate and distance traveled by the air sample and reagent prior to contact with the sensing mechanism, should be minimal.

TEMPERATURE COEFFICIENT

The instrument should be calibrated at different temperatures corresponding to actual operating conditions to determine the effect of temperature so that proper corrections can be applied. Instrumental methods employing reagent and

detection systems that vary as little as possible with temperature should be selected. Many methods of analysis and systems of detection are sensitive to temperature, and thermostatic regulation is required to minimize this source of error.

INSTRUMENT DRIFT

Changes in zero and span or gain settings should be minimal to avoid errors in the recordings and frequent calibration. Limitation of drift to a maximum of 1 percent in a 24-hour period would be desirable. Excessive electronic noise interferes with the interpretation of results. Unfortunately, in many instruments, noise level varies directly with sensitivity so that noise level will affect the maximum sensitivity attainable. Limitation of noise level to a maximum of 1 percent of full scale would be desirable.

FLOW OR PRESSURE REGULATION

Nonuniform airflow or pressure, and reagent flow, where appropriate, may produce serious errors in the analysis since the concentration recorded is a function of the quantity of air sampled (except in closed-path instruments). This is especially important when comparatively low flows are employed, since changes in flow would result in a higher percentage of error. For this reason, constant-flow devices should be employed, and flow rates should be automatically recorded. Calibration curves of variation of concentration with flow should be prepared, and the instrument should be operated under sampling conditions least affected by flow variations.

INSTRUMENT MAINTENANCE REQUIREMENT

The instrument should be constructed in such a manner as to require the minimum amount of attention and should be designed for simple maintenance. Parts that require more frequent replacement or servicing should be easily accessible. Complete instructions and diagrams for maintenance and trouble-shooting should be provided. No more than 1 day per week of attended operation would be desirable.

RECOMMENDED METHODS

Recommended Methods For Manual Sampling and Analysis

WEST AND GAEKE METHOD[1]

Introduction

The West-Gaeke method is applicable to the determination of sulfur dioxide (SO_2) in outside ambient air in the concentration range from about 0.005 to

5 ppm[1] SO_2 in the air sample is absorbed in 0.1 molar sodium tetrachloromercurate. Nonvolatile dichlorosulfitomercurate ion is formed in this process. Addition of acid-bleached pararosaniline and formaldehyde to the complex ion produces red-purple pararosaniline methylsulfonic acid, which is determined spectrophotometrically.[2] The system obeys Beer's law up to about 10 microliters of SO_2 per 10 milliliters of absorbing solution. This method is more sensitive than the hydrogen peroxide method and is not subject to interference from other acidic or basic gases or solids such as SO_3, H_2SO_4, NH_3, or CaO; the analysis should, however, be completed within 1 week after sample collection, and the concentrations of ozone and NO_2 should be less than that of the SO_2.[3,4,5]

Reagents

All chemicals used must be A. C. S. analytical-reagent grade.

Absorbing Reagent, 0.1 Molar Sodium Tetrachloromercurate. Dissolve 27.2 grams (0.1 mole) mercuric chloride and 11.7 grams (0.2 mole) sodium chloride in 1 liter of distilled water. (CAUTION: Highly poisonous; if spilled on skin, flush off with water immediately.) This solution can be stored at room temperature for several months.

Pararosaniline Hydrochloride (0.04%), Acid Bleached. Dissolve 0.20 gram of pararosaniline hydrochloride in 100 milliliters of distilled water and filter the solution after 48 hours. This solution is stable for at least 3 months if stored in the dark and kept cool. The pararosaniline used should have an assay of better than 95 percent and an absorbance maximum at 543 or 544 millimicrons. Pipette 20 milliliters of this into a 100-milliliter volumetric flask. Add 6 milliliters of concentrated HCl. Allow to stand 5 minutes, then dilute to mark with distilled water. This solution should be pale yellow with a greenish tint. It can be stored at room temperature in an amber bottle for a week or for about 2 weeks if refrigerated.

Formaldehyde, 0.2 Percent. Dilute 5 milliliters of 40 percent formaldehyde to 1,000 milliliters with distilled water. Prepare weekly.

Standard Sulfite Solution. Dissolve 640 milligrams sodium metabisulfite (assay 65.5% as SO_2) in 1.0 liter of water. This yields a solution of approximately 0.40 milligram per milliliter as SO_2. The solution should be standardized by titration with standard 0.01 normal I_2 with starch as indicator, and should be adjusted to 0.0123 normal. Then 1 milliliter = 150 microliters SO_2 (25°C, 760 millimeters Hg). Prepare and standardize freshly.

Starch Solution (Iodine Indicator), 0.25 Percent. Make a thin paste of 1.25 grams of soluble starch in cold water and pour into 500 milliliters of boiling water while stirring. Boil for a few minutes. Keep in glass, stoppered bottle.

Standard Iodine Solution, 0.01 Normal. Dissolve 12.69 grams of resublimed iodine in 25 milliliters of a solution containing 15 grams of iodate-free KI; dilute to the 1,000-milliliter mark in a volumetric flask. Pipette exactly 100 milliliters of this 0.1 normal solution and dilute to 1,000 milliliters in a volumetric flask with 1.5 percent KI. This solution can be used as a primary standard if the weighing is carefully done, or it can be checked against a standard thiosulfate solution. This solution should be stored in an amber bottle, refrigerated, and then standardized on the day of use.

Apparatus

Absorber. An all-glass midget impinger or other collection device capable of removing SO_2 from an air sample using 10 milliliters of absorbing reagent should be used. (Among the suppliers of midget impingers are Corning Glass Company and Gelman Instrument Company.)

Air Pump. The air pump should be capable of drawing 2.5 liters per minute through the sampling assembly.

Air-Metering and Flow Control Devices. Metering and control devices should be capable of controlling and measuring flows with an accuracy of $\pm$ 2 percent. The flow meter should be calibrated for variations in reading with temperature and pressure of the airstream so that the appropriate corrections can be applied.

Thermometer (or other Temperature-Measuring Device). The thermometer should have an accuracy of $\pm$ 2°C.

Mercury Manometer (or other Vacuum-Measuring Device). The manometer should have an accuracy of 0.2 inch Hg.

Spectrophotometer or Colorimeter. Color-measuring devices should be capable of measuring color intensity at 560 millimicrons, in absorbance cells 1 centimeter or larger.

Analytical Procedure

Collection of Samples. Set up a sampling train consisting of, in order, absorber, trap to protect flow device, flow control and metering devices, temperature and vacuum gauge, and air pump. All probes and tubing upstream from the bubbler should be pyrex glass, stainless steel, or teflon. Butt-to-butt connections may be made with tygon tubing. The downstream flow metering device can be empirically corrected to atmospheric conditions by conducting a dummy run with an upstream flowmeter inline that is open to the atmosphere.

Pipette exactly 10 milliliters of absorbing reagent into the absorber. Aspirate the air sample through the absorber at a rate of 0.2 to 2.5 liters per minute

(depending upon the concentration of SO_2 in the atmosphere and the sampling time desired). The sampling time may vary from a few minutes to 24 hours. For 24-hour sampling the absorber selected should be capable of containing 20 milliliters or more of absorbing reagent. For best results, the sampling time and rate should be chosen to provide a concentration of approximately 2 to 4 microliters of SO_2 in 10 milliliters of the absorbing reagent. The dichlorosulfitomercurate formed may be stored for 3 days with only a slight decrease in strength (about 1 percent per day). If samples are stored for longer periods, a correction factor should be applied. The sample may be stored in the collection device or transferred to a stoppered glass or polyethylene container.

Analysis. If a mercury precipitate is present owing to the presence in the air sample of inorganic sulfides, thiols, or thiosulfates, it may be removed by filtration or centrifugation. To the clear sample, adjusted to 10 milliliters with distilled water to compensate for evaporative losses, add 1.0 milliliter of acid-bleached pararosaniline solution and 1.0 milliliter of the 0.2 percent formaldehyde solution and mix.

Treat a 10-milliliter portion of unexposed sodium tetrachloromercurate solution in the same manner for use as the blank. If the collecting reagent remains exposed to the atmosphere during the interval between sampling and analysis, the blank should be exposed in the same manner.

Allow 20 minutes for maximum color development and read the absorbance at 560 millimicrons in a spectrophotometer with the blank as reference.

Calculations. Convert the volume of air sampled to the volume at standard conditions of 25°C, 760 millimeters Hg:

$$V_s = V \times \frac{(P - P_m)}{29.97} \times \frac{298.2}{(t + 273.2)}$$

V_s = Volume of air in liters at standard conditions
V = Volume of air in liters as measured by the meter
P = Barometric pressure in inches of mercury
P_m = Suction at meter in inches of mercury
T = Temperature of sample air in degrees centigrade.

Ordinarily the correction for pressure is slight and may be neglected.

Compute the microliters of SO_2 in the sample by multiplying the absorbance by the slope of the calibration plot. Then the concentration is:

$$\text{ppm } SO_2 \text{ by volume} = \frac{\mu l\ SO_2}{V_s}$$

Preparation of Calibration Curve

Pipette exactly 2 milliliters of standard sulfite solution into a 100-milliliter volumetric flask and dilute to mark with absorbing reagent. This final solution contains 3.0 microliters SO_2 per milliliter.

Add accurately 0.5-, 1.0-, 1.5- and 2.0-milliliter portions of the dilute standard sulfite solution to a series of 10-milliliter volumetric flasks and dilute to the marks with absorbing reagent. Continue with the analysis procedure given above.

Plot the absorbance (optical density) as the ordinate against the microliters of SO_2 per 10 milliliters of absorbing solution on rectangular coordinate paper. Compute slope of straight line best fitting the data.

Discussion of Procedure

The error for the combined sampling and analytical technique is $\pm$ 10 percent in the concentration range below 0.10 ppm with increasing accuracy with concentration in the range 0.1 to 1 ppm.

The measurements should be reported to the nearest 0.005 ppm at concentrations below 0.15 ppm and to the nearest 0.01 ppm above 0.15 ppm. O_3 and NO_2 interfere if present in the air sample at concentrations greater than SO_2.[4] Interference of NO_2 is eliminated by including 0.06 percent sulfamic acid in the absorbing reagent.[6] This may, however, result in a different calibration curve of lower sensitivity and in greater losses of SO_2 on storage of the sample for more than 48 hours after sample collection. NO_2 interference may also be eliminated by adding o-toluidine subsequent to sample collection.[7]

Heavy metals, especially iron salts, interfere by oxidizing dichlorosulfitomercurate during sample collection. This interference is eliminated by including ethylenediaminetetracetic acid in the absorbing reagent.[7] Sulfuric acid or sulfate do not interfere. There is no experimental evidence to indicate that SO_3 interferes; it probably hydrolizes preferentially in the absorbing reagent to form H_2SO_4 rather than combines with sodium tetrachloromercurate to form the dichlorodisulfitomercurate complex ion. If the latter reaction should prevail, SO_3 would interfere positively. If large amounts of solid material are present, a filter may be used advantageously upstream; however, a loss of SO_2 may occur.[8]

The color produced is independent of temperature in the range 11 to 30°C and is stable for 3 hours.

Much difficulty with the method has been caused by the use of impure pararosaniline hydrochloride.[9] A commercial brand is now available that is

GPO 813-685-2

specially selected for this procedure (Fisher Scientific Company, catalog No. P-389). The purity of the reagent may be estimated by comparing the slope of the calibration plot with the value 0.15 absorbance unit per microliter (obtained with 1-centimeter cells in a Cary spectrophotometer), which corresponds to a molar absorptivity of 36,700.

HYDROGEN PEROXIDE METHOD

Introduction

This method is applicable to the determination of SO_2 in outside ambient air in the concentration range from about 0.01 to 10.0 ppm. SO_2 in the air sample is absorbed in 0.03 normal hydrogen peroxide (H_2O_2) reagent (adjusted to about pH 5).[10,11] The stable and nonvolatile sulfuric acid formed in this process is titrated with standard alkali. The method requires only simple equipment and can be performed by analysts having lesser skills; it is preferable to the West-Gaeke method if SO_2 is the principal acid or basic atmospheric gaseous pollutant and if long storage of samples (greater than 1 week) prior to analysis is required.

Reagents

All chemicals used must be A. C.S. analytical-reagent grade.

Absorbing Solution, Hydrogen Peroxide, 0.03 Normal, pH 5. Dilute 3.4 milliliters of 30 percent H_2O_2 solution to 2 liters with distilled water. Determine the alkalinity of the solution by taking a 75-milliliter portion, adding 3 drops of mixed indicator, and adding approximately 0.002 normal HCl or HNO_3 from a buret until the indicator turns pink (pH 5). Calculate the amount of acid necessary to adjust the acidity of the bulk of the absorbent and add the required amount. The zero blank, obtained by titrating 75 milliliters of the adjusted reagent with 0.002 normal NaOH to the indicator equivalence point (green), should be not more than 2 drops. The reagent is stable at room temperature for at least 1 month.

Mixed Indicator, 0.1 Percent. Dissolve 0.06 gram bromocresol green and 0.04 gram methyl red in 100 milliliters of methanol. When stored in an amber bottle at room temperature the reagent is stable for at least 6 months.

Standard Sulfuric Acid Solution, 0.002 Normal. Prepare this solution by appropriate dilution of concentrated sulfuric acid. Standardize by the gravimetric barium sulfate method with a 200-milliliter portion or with a primary standard such as $Na_2B_4O_7 \cdot 10\ H_2O$. This reagent may be stored indefinitely without change in strength.

Standard Sodium Hydroxide Solution, 0.002 Normal. Prepare 2 liters of this solution by dilution of 1 normal sodium hydroxide with freshly boiled (CO_2-free) distilled water. Standardize as follows: Pipette 25 milliliters of standard sulfuric acid solution into an Erlenmeyer flask, add 3 drops of mixed indicator solution, and titrate with the sodium hydroxide reagent contained in a buret to the green equivalence point. Store the reagent in a polyethylene or other alkali-resistant bottle and restandardize bimonthly.

1 ml of 0.002 N NaOH = 64 μg SO_2 = 24.47 μl SO_2 (25°C, 760 mm Hg).

Apparatus

Absorber. A standard all-glass impinger or fritted bubbler is acceptable (capacity about 300 milliliters). (Among the suppliers are Corning Glass Company and Fisher Scientific Company.)

Air Pump. The pump should be capable of drawing 1 cfm through the sampling assembly.

Thermometer (or Other Temperature-Measuring Device). Thermometer should be capable of controlling and measuring flows with an accuracy of ± 2 percent. The flow meter should be calibrated for variation in reading with temperature and pressure so that the appropriate corrections can be applied.

Thermometer (or Other Temperature-Measuring Device). Thermometer should have an accuracy of ± 2°C.

Mercury Manometer (or Other Vacuum-Measuring Device). Manometer should have an accuracy of 0.2 inch Hg.

Buret. A buret of 25- or 50-milliliter capacity graduated in 0.1-milliliter subdivisions, preferably with teflon plug, should be capable of measuring volume with an accuracy of 0.05 milliliter.

Analytical Procedure

Collection of Samples. Set up a sampling train consisting of, in order, impinger, trap to protect flow device, flow control device, flow-metering device, temperature and vacuum gauge, and air pump. Measure 75 milliliters of absorbing reagent into the large impinger. Aspirate air through the bubbler at a rate of 1 cfm for 30 minutes. Note the readings of the vacuum gauge and thermometer. The downstream flow-metering device can be empirically corrected to atmospheric conditions by conducting a dummy run with an upstream flow meter inline that is open to the atmosphere. If an integrated 24-hour air sample is desired the sampling rate may be reduced to 1 liter per minute. For SO_2 concentrations of 0.3 ppm and greater the strength of the

standard alkali may be increased or the sampling time shortened. For concentrations greater than 0.8 ppm a second impinger should be connected in series so that a recovery efficiency of 98 percent is maintained. All probes and tubing upstream from the impinger should be pyrex glass, stainless steel, or teflon. Butt-to-butt connections may be made with short lengths of tygon tubing. The collected sample will not decompose on standing; consequently, the solution may be titrated long after sample collection. The sample may be stored in the impinger, which has been stoppered or transferred to a stoppered glass or polyethylene container.

Titration. Add three drops of mixed indicator solution and titrate the solution with standard 0.002 normal sodium hydroxide until the color changes from red to green. A reagent blank is titrated in the same manner, and this result (which should be less than 0.1 milliliter) is subtracted from the sample titer.

Calculations. Convert the volume of air sampled to the volume at standard conditions of 25°C, 760 mm Hg:

$$V_s = V \times \frac{(P - P_m)}{29.97} \times \frac{298.2}{(t + 273.2)}$$

V_s = Volume of air in liters at standard conditions
V = Volume of air in liters as measured by the meter
P = Barometric pressure in inches of mercury
P_m = Suction at meter in inches of mercury
T = Temperature of sample air in degrees centigrade.

Results are computed on the basis of the following reaction:

$$SO_2 + H_2O_2 \longrightarrow H_2SO_4$$

Thus the net titer of 0.002 normal NaOH (in milliliters) multiplied by 24.47 gives the microliters of sulfur dioxide. Then the concentration is:

$$\text{ppm } SO_2 \text{ by volume} = \frac{\mu l \ SO_2}{V_s}$$

Discussion of Procedure

The error for the combined sampling and analytical technique is ± 10 percent in the concentration range below 0.1 ppm with increasing accuracy with concentration in the range 0.1 to 1 ppm. The measurements should be reported to the nearest 0.01 ppm.

The presence in the air sample of strong acidic gases other than SO_2 or reactive acid solids such as HCl and $NaHSO_3$ gives erroneously high results, whereas the presence of alkaline gases or reactive basic solids such as NH_3 and CaO gives erroneously low results. H_2SO_4 does not interfere since it is not appreciably separated from the airstream owing to its small particle size except, perhaps, when the relative humidity is greater than 85 percent, which could result in particle sizes of greater than 1 micron. SO_3 gas, if present,

would be a positive interference. Sulfates do not interfere. CO_2 does not interfere since it is not absorbed in the acid-absorbing reagent. If large amounts of solid material are present, a filter may be employed advantageously upstream; however, a loss of SO_2 may occur.[8] The extent of this loss would depend upon the composition of the particulate matter and the nature and retentive capacity of the filter used. The acid base indicator is not included in the absorbing reagent because it tends to decompose during sampling, which leads to unreproducible results.

Recommended Procedure and Specifications for Automatic Monitoring Instrument

ELECTROCONDUCTIVITY ANALYZER*

Introduction

This method is applicable to the continuous, automatic sampling, analyzing, and recording of SO_2 concentrations in outside ambient air in the concentration range from about 0.01 to 2 ppm. The upper limit can range from 1 to 20 ppm, depending upon reagent flow and airflow rates and on electronic amplification. Air is continuously admitted to the absorber where the SO_2 in the airstream is removed by a continuously flowing liquid absorbent. The electrical conductivity of the resulting solution is continuously measured and recorded, and the readings obtained are proportional to the concentration of SO_2 in the sampled air. The method is not specific for SO_2 since other soluble electrolyte-forming gases and solids affect the results.

Reagents

All chemicals used must be A. C. S. analytical-reagent grade.

Distilled Water. For use as absorbing solution, distilled water should be prepared by passing it through a cation-anion exchange resin.

Hydrogen Peroxide-Sulfuric Acid, Alternate Absorbent, 2×10^{-3} molar H_2O_2, 1×10^{-5} normal H_2SO_4. Add 2.3 milliliters of 3 percent H_2O_2 solution per liter of 1×10^{-5} normal H_2SO_4.

---

* It is not intended to imply that only analyzers using electroconductivity detectors are suitable for automatic monitoring of SO_2 in air. At the time of this report, electroconductivity analyzers most nearly fulfilled the criteria for evaluation and the recommended instrument performance specifications set forth herein. Further research on and development of automatic air-monitoring instruments incorporating other principles of detection such as potentiometry, photometry, air ionization, thermal conductivity, and so forth should be encouraged as well as electroconductivity.

2, 4, 5 Trichlorophenate (Dowicide B) or Any Suitable Fungicide. Add 2 milligrams of absorbing reagent per liter.

Calibration Reagent. A reagent should be prepared corresponding to 1 ppm SO_2 under the conditions of air sample flow rates employed. Add the calculated amount of 0.1 normal H_2SO_4 solution to 1 liter of unexposed absorbing reagent.

Apparatus

The apparatus should consist of a suitable assembly of sampling probe, absorber, regulating and recording device for airflow, regulating and recording device for liquid flow, air pump, liquid-metering pump or constant-head device with capillary tube for dispensing the absorbent at a constant rate, thermostatted cabinet, conductivity electrodes, and conductivity recorder.

Sampling Probe. The sampling probe should be made of pyrex glass, 316 stainless steel or teflon tube with intake end turned down, and a loose glass wool filter to remove large particulate matter. The inline prefilter should be mounted indoors, exterior to the instrument, or, if necessary, inside the thermostatted cabinet, to prevent condensation of water vapor, which would absorb SO_2 and result in serious losses.

Absorber. A venturi scrubber or any reagent-air-contacting system capable of a scrubbing efficiency of 98 percent or more is acceptable.

Measuring, Regulating, and Recording Device for Airflow. A flowmeter, needle valve, or other flow-measuring, flow-regulating device capable of measuring flows with an accuracy of $\pm$ 2 percent should be used. The airflow rate should be monitored continuously by means of suitable mechanical and electronic circuitry to cause characteristic markings to appear on the conductivity recorder chart.

Measuring, Regulating, and Recording Device for Liquid Flow. A metering pump, flowmeter, and needle valve or device capable of measuring flows with an accuracy of $\pm$ 2 percent is acceptable. The liquid flow rate should be monitored continuously by means of suitable mechanical and electronic circuitry to cause characteristic markings to appear on the conductivity recorder chart.

Air and Liquid Pumps. Any air pump and liquid pump or combination air-liquid pump is acceptable that is capable of drawing air at a rate of 5 liters per minute and liquid at a rate up to 30 milliliters per minute through the absorption-analyzing system under conditions of continuous operation. To assure satisfactory performance, the pump should have a much greater capacity, about 20-liters-per-minute airflow under the conditions of operation.

Thermostatted Cabinet. The reagent feed lines, absorption column, and conductivity cells should be enclosed in an insulated compartment thermostatically maintained at a temperature a few degrees higher than the highest ambient temperature expected. The temperature of the reagent in the conductivity cells should be continuously monitored by means of suitable electronic circuitry to cause characteristic markings to appear on the conductivity recorder chart.

Conductivity Electrodes. Two sets of platinum dip electrodes of suitable dimensions, one pair to measure the conductivity of the unreacted reagent and the other that of the reacted reagent, should be provided.

Conductivity Recorder. A zero-to-10 millivolt, potentiometric, strip chart recorder with 30-day chart and scale graduated from zero to 100 and chart speed of 1 or 2 inches per hour, or any instrument capable of recording the differential output of the conductivity cells corresponding to an SO_2 concentration range of zero to 2 ppm with an accuracy of $\pm$ 1 percent of full scale should be provided.

Reagent Reservoir and Delivery Bottle. Any bottle with sufficient volume to contain a 1 week's supply of reagent can be used; the reagent should be protected from air pollutants by the insertion of a soda-lime charcoal column on the air inlet line.

Switch-controlled Electronic Check. A switch-controlled manual check containing the proper resistance to cause a deflection of the recorder corresponding to a concentration of 1 ppm SO_2 should be used.

Switch-controlled Electronic Zero Check. A check should be used to simulate a differential conductivity between the reference cell and a known resistance equivalent to zero ppm SO_2. This also serves as a check on the purity of the unreacted reagent.

Calibration

Static Calibration, Standard Solutions. The instrument may be calibrated by sulfuric acid solutions of known composition corresponding to definite atmospheric SO_2 concentration in the range zero to 2 ppm. Solutions corresponding to 0.5, 1.0, 1.5, and 2.0 ppm SO_2 are prepared by the addition of calculated amounts of 0.1 normal H_2SO_4 to the absorbing reagent. The static methods described below may be used when the absorption efficiency is known to be greater than 98 percent.

1. Establish instrument zero by introducing the unexposed absorbing reagent in both the reference and sample conductivity cells; then the

standard solutions are substituted for the absorbing reagent in the sample conductivity cell only. The instrument reading is checked against the standard reagent, and if necessary, the instrument is adjusted by means of the span control to indicate the correct concentration.

2. The standard solution is substituted for the absorbing reagent and is introduced directly into the system as in normal operation. SO_2-free air, obtained by passage of air through a drying tower containing ascarite or soda lime, is admitted to the analyzer under the same conditions as in actual sampling. The instrument reading is checked against the standard reagent, and the necessary corrections are made. Absorbing reagent is maintained in the reference cell.

Dynamic Calibration, Standard Gas Mixture. The dynamic calibration methods described below should be employed to take into account the scrubbing efficiency of the absorbing column under flow conditions. Standard air-SO_2 mixtures may be prepared in a rigid test chamber, compressed gas cylinder, or collapsible mylar or other inert plastic bag and then introduced into the analyzer. The mixtures are prepared by diluting a measured quantity of pure SO_2 gas with a known volume of SO_2-free air. A measured quantity of SO_2 gas may be introduced into the test chamber through a rubber diaphragm by means of a hypodermic syringe and needle. In the compressed-gas-cylinder technique, the dilution of SO_2 is accomplished by introducing a measured amount of SO_2 by a hypodermic syringe into a partially evacuated, stainless steel cylinder and compressing the mixture by addition of air contained in a compressed-air cylinder at high pressure until the desired pressure is reached. When a rigid test chamber is employed, corrections should be applied for the diminution of gas concentration resulting from the dilution of the test gas by influent air during sampling, or a flexible plastic bag can be put inside the chamber to receive replacement air. The concentration of SO_2 in the gas streams prepared by the above methods should be calibrated by the West-Gaeke or hydrogen peroxide methods.

The instrument may also be calibrated against a manual method such as the West-Gaeke or the hydrogen peroxide method. Atmospheric air or synthetically produced air-SO_2 mixtures are introduced simultaneously into the analyzer and the manual absorber. The instrument record is adjusted to read SO_2 concentrations as determined by the manual method.

Fluctuations in air-liquid flow rate and temperature may occur. Calibration curves showing the effect of these variations on recorder reading should be prepared so that appropriate correction factors can be applied.

Procedure

(a) When a fresh supply of absorbing solution is installed in the apparatus, any air bubbles that may form in the reagent feed lines must be removed.

(b) Check the airflow and liquid flow rates and temperature of the reagent in the conductivity cells and make necessary adjustments.

(c) Check the ink supply to the pens in the recorder. Check the recorder battery and output range by suitable electronic test equipment.

(d) Lubricate the pump and motors as required.

(e) Calibrate the instrument once a week or more or less frequently as required.

(f) Interpret the charts by using a calibration curve on a section of the recorder paper, or integrate under the curve by using a planimeter. Correct for deviations from the standard curve due to variations in temperature and airflow or liquid flow. Hourly concentrations may be used to calculate time-concentration values. Short-time peak concentrations are measured as required.

Instrument Performance Specifications*

(a) A reproducibility of ± 1 percent of full-scale deflection over a 24-hour period,

(b) an instrument accuracy of ± 2 percent of full-scale deflection over a 24-hour period,

(c) linear response in all ranges of concentration (90% response time not to exceed 1 minute for the concentration range zero to 2 ppm),

(d) electronic drift not to exceed 1 percent of full scale in 24 hours,

(e) zero to 2 ppm full-scale range with a sensitivity of 0.01 ppm,

(f) sufficient control of temperature, reagent, and sample flows to assure the accuracy of the calibration technique.

---

* Electroconductivity analyzers are available from the following manufacturers: Beckman Instrument Company, Davis Emergency Equipment Company, Leeds & Northrup, Instrument Development Company, Mervyn-Cerl Ltd., and distributed by Gelman Instrument Company. Not all models supplied by manufacturers meet these performance requirements. In the case of some of the manufacturers none of the models available as of January 1964 meet specifications.

GPO 813-685-3

Discussion

Electroconductivity, which is measured in terms of the resistance of the solution between two electrodes immersed in it, is a property of all ionic solutions and is not specific for any particular compound. It is dependent upon the number and type of ions dissolved in solution. Soluble gases that yield electrolytes in solution cause the greatest interference. All hydrogen halides present would be measured. Except near special sources of contamination, these gases are, however, seldom present in air in appreciable amounts in comparison with SO_2. Weak acidic gases such as H_2S cause practically no interference because of their slight solubility and poor conductivity. If the water is free of bases, the carbon dioxide content of air causes no interference. Alkaline gases, such as ammonia, interfere by neutralizing the acid and yield comparatively low results because the transport number of the hydrogen ion is several times greater than that of other cations. Similarly, lime dusts or other basic solids, if absorbed, would cause comparatively low results for SO_2. Neutral and acidic aerosols such as sodium chloride or sulfuric acid would give comparatively high results depending on their solubility, ionization, and the ability of the absorption system to remove them from the airstream, which, in this method, is very poor unless particle size is relatively large. Since the particle size of sulfuric acid mist is small (less than 1 μ) except perhaps when the relative humidity is greater than 85 percent, it is not measured appreciably in this method. A special absorber and different operating parameters are required for effective collection of sulfuric acid mist. A loose glass wool filter is used to minimize maintenance time requirements for cleaning of absorber and conductivity cells, and reducing the interference of particulate matter. SO_3 gas, if present, would result in a positive interference. Instrument response is a function of gas concentration, airflow and liquid flow rate, and conductivity cell constants. Response time is a function of liquid flow rate and the distance and volume between the absorber and the conductivity cells.

A change in temperature of 2°F will alter the conductivity of a strong electrolyte by approximately 2 percent; consequently, for accurate operation, the absorption column and conductivity cells should be enclosed in an insulated compartment thermostatically maintained at a temperature a few degrees higher than the maximum ambient temperature expected.

Perley and Langsdorf [12] reported that, at SO_2 concentrations of 2 ppm, amounts of CO_2 as high as 2,000 ppm had no influence on the resultant SO_2 measured. H_2S concentrations of 25 ppm result in a positive reading of 0.2 ppm. Since this concentration is rarely approached in atmospheric sampling the interference of this weak acid is not appreciable.

Yocom et al. [13] reported on the effect of hydrogen chloride on the operation of an electroconductivity analyzer. Concentrations of hydrogen chloride in the

range 1.2 to 11.4 ppm were collected at an efficiency of 75 percent. The relationship between concentration of HCl and its equivalent concentration in ppm SO_2 was 1:2.9. From these considerations it was shown that appreciable interference is caused by the presence of HCl, as would be the case with all hydrogen halides and other strong electrolytes.

Jacobs, Braverman, and Hochheiser [14] adapted an electroconductivity analyzer to the measurement of SO_2 in outside air in the concentration range zero to 0.95 ppm full scale. A dynamic calibration procedure is described by the authors. Synthetic air-SO_2 mixtures are introduced into the instrument and into a bubbler containing the hydrogen peroxide reagent simultaneously. In this manner the instrument is standardized in terms of the acidimetric hydrogen peroxide method.

Reece, White, and Drinker [15] adapted the electroconductivity analyzer to the analysis of CS_2 and H_2S by attaching a combustion furnace and oxidizing these gases to SO_2. The apparatus was also used for the analysis of sulfur compounds and chlorinated hydrocarbons by Thomas et al. [16] Pyrolysis and oxidation to HCl and SO_2 were accomplished in a silica combustion tube by using a platinum catalyst.

A detergent solution may be added to the absorbing reagent to help maintain uniformity of liquid flow and prevent the accumulation of dust in the flow system. [17]

Commercially available electroconductivity analyzers designed for the measurement of SO_2 in air are described in a book about air-sampling instruments. [18]

Recommended instruments and procedures for automatic monitoring of SO_2 in air are contained in published methods manuals on atmospheric sampling and analysis. [19,20]

COMPARISON OF METHODS CONSIDERED

Manual Methods

Hochheiser and co-workers [21] compared the hydrogen peroxide, iodine, and fuchsin-formaldehyde methods for the determination of SO_2 in air by taking atmospheric samples in New York City and found that all were equally reliable (Table 1). In the peroxide method, the strongly acidic component

in the air is determined rather than acidity attributable to SO_2 alone, but there is little difference in the results obtained by these methods, particularly in the lesser concentrations, because the major acidic pollutant is SO_2.

Table 1. COMPARISON AMONG METHODS OF DETERMINING SO_2, ppm

Peroxide method	Iodine method	Fuchsin method
0.30	0.26	0.25
0.30	0.23	0.22
0.27	0.22	0.22
0.23	0.22	0.22
0.15	0.14	0.12
0.15	0.12	0.10
0.15	0.11	0.09
0.14	0.11	0.09
0.11	0.09	0.07
0.09	0.09	0.06
0.07	0.07	0.06
0.05	0.06	0.05
0.05	0.05	0.04
Average		
0.15	0.13	0.12

In accordance with a recommendation of the working party to study methods of measuring air pollution used by the organization for European Economic Co-operation, the United Kingdom delegation made comparisons among four recognized methods of estimating SO_2 on a simple routine basis.[22] The West-Gaeke, peroxide, Stratman, and direct iodine methods were compared by means of atmospheric samples obtained at a measuring site in a city center during the winter period.

Table 2 shows that the hydrogen peroxide and the West-Gaeke methods gave fair agreement when used in routine measurement. The Stratman method yielded erratic results in that in some instances it gave good agreement with the two methods mentioned above, but sometimes its results varied considerably from those of the other two. Table 2 shows the tendency of the iodine method to read consistently high. This tendency appears to be owing to carryover of iodine from solution by the air stream.

Table 2. COMPARISON AMONG METHODS OF DETERMING SO_2, $\mu g/m^3$ (1 ppm = 3,000 $\mu g/m^3$)

West-Gaeke	Hydrogen peroxide	Stratman	Direct iodine
465	475	495	605
575	630	180	930
245	200	285	410
245	210	430	390
425	330	465	490
380	450	480	---
840	785	850	1,090
150	205	215	400
245	270	160	530
310	240	235	295
730	620	215	880
175	155	80	240
Average			
390	368	298	550

Welch and Terry[23] reported that values obtained by the H_2O_2 method were approximately 30 percent lower than values found by the West-Gaeke method for concentrations up to 0.65 ppm. The relationship between the West-Gaeke and the H_2O_2 method was established by using synthetic mixtures of SO_2 in air and a dynamic calibration procedure. It is believed that this should be investigated further since the collection efficiency of the H_2O_2 method is generally considered to be greater than 90 percent. Relatively close correlation between the electroconductivity analyzer and the West-Gaeke procedure was obtained on synthetic air-SO_2 mixtures in the range of 1 to 3 ppm.

Paulus, Floyd, and Byers[24] compared the polarographic method of analysis with the fuchsin-formaldehyde colorimetric method. The polarographic results consistently averaged from 2 to 7 percent less than the colorimetric results, depending upon the concentration range. A wider deviation was obtained in the lower concentration range.

Terraglio and Manganelli[4] studied the variability of the H_2O_2, West-Gaeke, and iodine methods. A comparative study over the concentration range of 0.10 to 1.3 ppm SO_2 prepared synthetically in a test chamber showed that the average results obtained by the acidimetric and colorimetric methods were approximately the same but results of a single determination could vary significantly.

Comparative recoveries by the iodimetric method were found to be lower than the values obtained by the above-mentioned methods. The relative percentage recovery by the acidimetric method compared with the West-Gaeke method was 106 percent at a concentration of 0.1 ppm and decreased to 97 percent at 1.3 ppm. For the iodimetric method, the relative percentage recovery increased from 70 percent of the colorimetric value at 0.1 ppm to 84 percent at 1.3 ppm SO_2. The presence of ozone-oxides of nitrogen interfered with all three methods as follows:

a. Colorimetric method resulted in reduced recovery owing to bleaching of the sample by oxides of nitrogen and ozone.

b. Acidimetric method resulted in increased recovery owing to titration of oxides of nitrogen dissolved in trapping solution.

c. Iodimetric method resulted in increased recovery owing to variation in the method of oxidation of the sulfur dioxide (Table 3).

Table 3. INFLUENCE OF OZONE-NITROGEN OXIDES ON THE DETERMINATION OF SO_2

Ozone added,	NO_2 added,	SO_2 added,	SO_2 recovered, ppm		
ppm			Colorimetric	Iodimetric	Acidimetric
0.01	0.07	0	0	0	0.03
0	0	0.47	0.47	0.25	0.48
0	0	0.46	0.46	0.38	0.44
0.01	0.07	0.47	0.44	0.20	0.53
0.08	0.25	0.46	0.38	0.36	0.69
0	0	0.47	0.47	0.26	0.49
0	0	0.46	0.46	---	0.51

Selection of the manual methods currently used by the Division of Air Pollution was based upon an evaluative review of available literature information reported herein and upon the experience of field investigators.

Reference to Table 4 and the material that follows it shows that of all the manual methods reviewed the West-Gaeke and hydrogen peroxide methods best approach the criteria for evaluation set forth herein. The West-Gaeke method has a higher sensitivity, but its calibration and analytical procedure are more difficult. The absorbents used and the products formed in the separation and concentration of the pollutant from the air mass are stable in both methods; though the product formed in the hydrogen peroxide method is more stable; either one may, therefore, be employed with automatic se-

Table 4. COMPARISON AMONG MANUAL METHODS FOR THE ANALYSIS OF SO_2 IN AMBIENT AIR

Method	Sensitivity, ppm	Accuracy, ± %, combined error sampling and analytical technique	Reproducibility, ± %	Interferences (known)	Sampling rate, liters/min.	Collection efficiency, %	Stability of absorbents, days	Stability of product, days
Colorimetric								
1. West-Gaeke	0.005	10	3	NO_2, O_3	1 to 4	95 to 100	90	3
2. Fuchsin-formaldehyde	0.01	10	3	NO_2, O_3, S, SH, S_2O_3	1 to 4	90 to 100	90	2
3. Stratman	0.01	--	--	H_2O, H_2S, SO_3	1 to 5	90 to 100	90	--
4. Barium chloranilate	0.05	--	--	PO_4, F, Cl	20 to 30	90 to 100	30	90
Impregnated test papers								
5. Zinc nitroprusside	0.5	20	10	HCl, H_2S, CS_2 only at high conc	0.30	--	90	2 hours
6. Astrazone pink	0.05	--	--	---	0.25	--	14	Read directly
Sulfate ion								
7. Diazo dye	0.20	10	3	PO_4, Cl, SO_3	1 to 4	90 to 100	90	90
8. Thorium borate-amaranth	0.5	20	10	F, PO_4, HCO_3, SO_3	1 to 4	90 to 100	90	90
9. Ultraviolet determination	0.03	--	--	H_2S, H_2SO_4	--	--	--	--
Acidimetric								
10. Hydrogen peroxide	0.01	10	3	Acid and alkaline gases	3 to 28	90 to 100	30	90
11. Polarographic	0.02	10	3	Oxidants	24	90 to 100	90	2
Iodimetric								
12. Iodine	0.01	10	3	Oxidizing and reducing materials	20 to 30	85 to 100	90	2
13. Direct iodine	0.10	15	5	Oxidizing and reducing materials	5	85 to 100	1	Read directly
14. Iodine thiosulfate	0.40	10	3	Oxidizing and reducing materials	5	85 to 100	1	1
15. Turbidimetric	0.40	10	3	Fluorides Particulates	20 to 30	90 to 100	90	90
Cumulative								
16. PbO_2 candle	0.02 mg SO_3/100 cm²/day	15	7	--(2 weeks' to 3 months' exposure)		--	90	90

quential sampling equipment. Comparable results are obtained by sampling and analyzing known amounts of synthetic mixtures of SO_2 in air. Both methods are nonspecific, though the West-Gaeke method is more selective, and further studies concerning the relative effects of interfering materials are necessary.

Instrumental Methods

The performance parameters of the automatic monitoring instruments are summarized in Table 5. Of the analyzers currently commercially available, some models of those employing the electroconductivity detection principle best approach the criteria for evaluation. Any instrument employing other methods of detection, such as potentiometry, photometry, and ionization, that meet the performance criteria established for the electroconductivity analyzer would also be acceptable. The experience of field investigators has demonstrated that the operating parameters specified for the automatic instrumental method selected for use that are detailed herein are necessary for satisfactory operation of the equipment over a reasonable period of unattended operation.

The method is nonspecific since any soluble, electrolyte-forming gases and solids affect the result. It has, however, been found that, except in special situations, the measurements recorded by these analyzers predominantly result from atmospheric SO_2.

MANUAL METHODS CONSIDERED IN ADDITION TO RECOMMENDED METHODS

Colorimetric Methods

FUCHSIN-FORMALDEHYDE METHOD[25]

SO_2 in the atmosphere is removed and concentrated by scrubbing through a sampling solution of 0.1 normal sodium hydroxide and 5 percent glycerol. The subsequent determination of SO_2 is based on a color reaction first developed by Steigmann.[26] The chromogenic reagent consists of a mixture of basic fuchsin, sulfuric acid, and formaldehyde, which develops a red-violet color in the presence of sulfurous acid.

Table 5. COMPARISON AMONG AUTOMATIC GAS ANALYZERS FOR THE CONTINUOUS RECORDING OF ATMOSPHERIC SO_2

Principle of operation[a]	Absorbent	Range covered, ppm	Sensitivity, ppm	Reproducibility, ppm	Interference	Stability of reagent, days
Electroconductivity						
1. Analyzer "A"	De-ionized water	0 to 2	0.01	0.02	Soluble ionic materials (i.e., acids, bases, salts)	Extremely stable; reagent is circulated through purification system.
2. Analyzer "B"	Hydrogen peroxide-sulfuric acid	0 to 5	0.05	0.10	"	30
3. Analyzer "C"	"	0 to 2	0.01	0.02	"	30
4. Analyzer "D"		0 to 1	0.02	0.05	"	30
Potentiometric	Potassium bromide-sulfuric acid	0 to 10	0.10	0.20	Oxidants and reductants i.e., H_2S, mercaptans, NO_2, O_3, etc., and olefins, phenols	Extremely stable; reagent is circulated through purification system
Photometric						
1. Analyzer "A"	Starch-iodide	0 to 1	0.01	--	Oxidants and reductants i.e., H_2S, NO_2, etc.	7
2. Analyzer "B"	"	0 to 1	0.01	--	"	7
3. Analyzer "C"		0 to 0.5	0.01	--	"	7
4. Analyzer "D"	Pararosaniline-formaldehyde	0 to 5	0.02	--	NO_2 and O_3 if present in appreciable quantities	14
Air ionization	Aerosol formation	0 to 10	--	--	--	--

a. Described in what follows.

The absorption maximum is at 570 millimicrons, and the color is independent of temperature in the range 23 to 26°C. Above this range the effect of temperature on the absorbance of the sample gives increasingly erroneous results. A 30-minute color development thermostatted at 25°C was suggested. The extent of color stability for longer periods was not reported.

Inorganic sulfides, thiols, and thiosulfates interfere with the determination and may be removed as a mercury precipitate by treatment with saturated mercuric chloride prior to the addition of the colorimetric reagent.[27]

The method has a sensitivity of 0.01 ppm with a 40-liter air sample scrubbed through 10.0 milliliters of absorbing solution. The minimum amount detectable is 0.1 microgram per milliliter of solution. At a sampling rate of 20 liters per hour with a midget fritted bubbler, the collection efficiency is close to 100 percent. Stang et al., [28] using a Greenburg-Smith all-glass impinger containing 100 milliliters of 1 percent glycerol in 0.05 normal sodium hydroxide and sampling at 1 cubic foot per minute, obtained results indicating from 93 to 99 percent efficiency based on the amount of SO_2 collected in two impingers in series.

Moore, Cole, and Katz [29] reported that NO_2, if present in the same concentration range as SO_2, produces a negative interference owing to the bleaching effect of NO_2 on the fuchsin-formaldehyde sulfite color. Corrections for the effect of NO_2 on the colorimetric SO_2 values were obtained by concurrent determination of SO_2 by the conductimetric and colorimetric methods and of NO_2 by the Saltzman method.

Paulus, Floyd, and Byers [24] found it necessary to establish a new standard curve with each new batch of colorimetric reagent. They also reported on the effect of aging, light, and agitation on the collected sample. Solution strength was determined after the first, third, and sixth days of sample collection. Average losses of 6 percent were found after 6 days. The samples that showed losses after the first and third days were mostly in the lowest concentration range. No losses due to sunlight or artificial light were found. The effect of agitation is important when samples are shipped by mail. Losses due to agitation are comparable to those due to the aging experiments and are, therefore, not hastened by this condition.

The fuchsin-formaldehyde method for the determination of SO_2 in air is recommended and reported in the ACGIH manual of recommended methods.[30] An average deviation of 8 percent was found. According to ACGIH, when concentrations of nitrogen oxides higher than those of SO_2 are anticipated, the polarographic method should be used.

STRATMAN METHOD[31]

Atmospheric SO_2 is initially absorbed on silica gel and then reduced with hydrogen to H_2S on a platinum contact catalyst at 700 to 900°C. The H_2S formed is passed into a bubbler containing 2 percent ammonium molybdate in 0.4 normal sulfuric acid. The resulting blue-violet molybdenum complex is then determined colorimetrically with the aid of a Ziess Opton S57 filter. According to the amount of reagent used, 1 to 200 micrograms of SO_2 can be determined. Efficiency of removal of atmospheric SO_2 is higher than 90 percent at a sampling rate up to 5 liters per minute. If the quantity of air sampled contains more than 300 milligrams of water, it must be dried by passage through a preliminary drying tower containing phosphorous pentoxide. It was found that pressures up to 200 millimeters Hg and temperatures between 18 and 40°C do not affect the collection efficiency. The method has a sensitivity of 0.01 ppm with a 40-liter air sample when the H_2S produced in the catalytic desorption process is absorbed in 10 milliliters of the ammonium molybdate reagent. The interference of SO_3 is eliminated by preceding the silica gel absorption equipment by a bubbler containing phosphoric acid. The Stratman method is particularly suitable for relatively short-term sampling since moisture interferes when samples are obtained over a longer time.

BARIUM CHLORANILATE METHOD[32,33]

The method is based on the reaction of solid barium chloranilate with sulfate ion at pH 4 in 50 percent ethyl alcohol to liberate highly colored acid-chloranilate ion. The concentration is determined spectrophotometrically with the absorption peak at 530 millimicrons. Atmospheric SO_2 is removed, concentrated, and oxidized to sulfate by scrubbing through 0.5 percent aqueous H_2O_2 solution. A buffer solution, 95 percent ethyl alcohol and 0.1 gram barium chloranilate, is added and the mixture is shaken for 10 minutes. The excess barium chloranilate and the precipitated barium sulfate are removed by filtration. The method has a sensitivity of 0.05 ppm with a 1,000-liter air sample scrubbed through 25 milliliters of absorbing solution. Kanno [32] reported a collection efficiency of close to 100 percent at a sampling rate of 5 liters per minute. The residual presence of H_2O_2 and CO_2 did not interfere with the colorimetric method. The accuracy and the effect of interfering materials were not reported. Phosphates, fluorides, and chlorides are known to interfere in the chloranilate procedure, and a preliminary separation would be required. A method for the conversion of the gravimetric lead peroxide method to colorimetric with the use of barium chloranilate is also described by the author.

ZINC NITROPRUSSIDE METHOD[34]

Air is aspirated at the rate of 300 milliliters per minute through a test paper supported in a suitable holder. The determination of SO_2 is based on

the formation of a brick-red stain, which is compared with a standard stain chart or with a disc of standard tints. The test papers are prepared by soaking strips of filter paper in ammoniacal zinc nitroprusside solution and drying at a temperature not exceeding 40°C. The dried test papers are stored in a stoppered container in the dark and are moistened by spraying with water immediately before use. It was found that dry zinc nitroprusside papers are stable indefinitely whereas papers prepared with glycerol decompose after about 4 weeks of storage.

With a 360-milliliter air sample, the range of concentrations determinable with an accuracy to within ±20 percent is 1 to 20 ppm. Hands and Bartlett[34] stated that concentrations outside these limits can be measured by increasing or decreasing the size of the sample. The stains are stable for about 2 hours. The effect of hydrogen chloride, hydrogen sulfide, and carbon disulfide on color production was investigated. Hydrogen chloride produced a discoloration while hydrogen sulfide produced a positive stain, although this effect was observed only at relatively large concentrations. Carbon disulfide at concentrations up to 500 ppm yielded no stain.

In an investigation of the starch-potassium iodide-potassium iodate test paper method[35] the authors found that, unless strict control was exercised during the preparation of the test paper, nonuniform papers resulted. This made the calibration of the procedure difficult.

ASTRAZONE PINK METHOD[36]

Air is drawn through a wet test paper at a rate of 250 milliliters per minute until bleaching of the impregnating reagent is effected whereupon the volume of air taken to produce this effect is noted. The test reagent consists of Astrazone Pink FG (Bayer), sodium bicarbonate, and glycerol and is stable in the dark for 2 weeks. The dye solution alone is unchanged after several months. One drop of this reagent is placed on the filter paper and allowed to spread before sampling. The method has a sensitivity of 0.05 ppm SO_2. No information is reported regarding the specificity or accuracy of the method.

DIAZO DYE METHOD

Klein[37] described a colorimetric method for the determination of sulfate ion that may be applicable to air analysis. The sulfate in the sample is precipitated as benzidine sulfate with benzidine hydrochloride, purified, dissolved in 0.2 normal HCl, diazotized, and coupled with N-1-naphthylethylenediaminedihydrochloride after excess nitrous acid is destroyed. The resultant purple color is read in a colorimeter with a green filter. The color produced is stable for at least 12 hours. Phosphate and chloride interfere in the determination. Phos-

phate should be completely removed. If the ratio of chloride to sulfate is greater than 30, incomplete precipitation of benzidine sulfate occurs. The sensitivity of the method is 0.05 milligram in 15 milliliters of sample solution, or to translate this to air sample concentration, the sensitivity would be 0.2 ppm for a 90-liter air sample collected in a midget impinger containing H_2O_2-absorbing reagent. Comparison with the gravimetric sulfate method shows good correlation of results. The analytical error is ± 2 percent.

THORIUM BORATE-AMARANTH DYE METHOD

A colorimetric procedure for determining sulfate ion, described by Lambert et al. [38] uses an insoluble thorium borate-amaranth dye reagent. This procedure may be applicable to air analysis. Sulfate releases dye molecules from the solid reagent in direct proportion to the concentration of the dye measured at 521 millimicrons. Interference by fluoride, phosphate, and bicarbonate is eliminated through the use of lanthanum ion and a weak acid cation exchange resin. It was found that the color produced was independent of the amount of reagent added and a function only of the sulfate ion in solution. Nevertheless, it was found necessary to prepare a calibration curve for each new batch of reagent. Reaction time is not a factor in the range 1 to 10 minutes. With a 10-millimeter cell path, the sensitivity of the method is 0.2 milligram sulfate contained in 10 milliliters of sample with a reproducibility of 10 percent. For a 90-liter air sample obtained by collection and oxidation of SO_2 to SO_4 the sensitivity would be 1 ppm. No doubt the sensitivity of the method could be increased by increasing the cell path.

INDIRECT ULTRAVIOLET DETERMINATION OF SO_2 BY MEANS OF PLUMBOUS ION [39]

SO_2 is precipitated as lead sulfite with 1 milliliter of lead acetate solution (100 μg/ml) and is determined indirectly as the plumbous ion remaining in solution at 208 millimicrons. Plumbous ion absorbs at 208 millimicrons (molar absorbance 8,210) and this permits a sensitivity of 13 micrograms of plumbous ion per 0.1 absorbance unit (equivalent to 8 μg SO_2) to be attained. The lead precipitate is sufficiently insoluble in water at room temperature for plumbous ion not to be spectrophotometrically determinable from its saturated aqueous solution.[40] This method would be sufficiently sensitive for atmospheric analysis and may be applicable to air analysis by scrubbing an air sample through a suitable absorbent and subsequently using the indirect, ultraviolet, spectrophotometer method.

Blinn and Gunther [39] found that under the conditions specified, two moles of SO_2 are needed to precipitate 1 mole of plumbous ion. Acid gases such as H_2S and H_2SO_4, which precipitate plumbous ion from aqueous solutions, and other materials, which absorb strongly in the 250- to 190-millimicron region, would interfere.

FERROUS-PHENANTHROLINE METHOD

Stephan and Lindstrom [41] developed a direct color method for determining SO_2 in the atmosphere. The air sample is passed through a wet scrubber containing ferric-phenanthroline reagent. Sulfite ion oxidizes ferric ion to ferrous and produces the colored ferrous-phenanthroline complex ion.

The color produced is stable for about 3 days. Nitrogen dioxide and ozone do not interfere. The lower limit of detection is 0.05 ppm for a 100-liter air sample collected for 50 minutes in 75 milliliters of absorbing reagent. A serious disadvantage of the method is that the relatively high temperature sensitivity during sampling necessitates the use of a constant water bath or other regulatory device to control temperature to $\pm$ 0.5°C. Because of the stability of the product formed, this method can, however, be adapted for use with a sequential sampler or for collection of an integrated 24-hour sample provided that the sampling unit is thermostatted.

POLAROGRAPHIC METHOD [24]

SO_2 in air is removed and concentrated by scrubbing through an absorbing solution, contained in a standard, all-glass, Greenburg-Smith impinger, consisting of 2 percent glycerol in 0.05 normal sodium hydroxide at a rate of 24 liters per minute for 30 minutes. Subsequently an acetate buffer (pH 4) is added, and the combined solution is deaerated by bubbling nitrogen through the sample contained in an air electrolysis vessel. The flow of nitrogen is then stopped, and a polarogram is made from -0.35 to -1.00 volt. A sensitivity of 0.006 microampere per millimeter is used.

For a 30-minute air sample contained in 75 milliliters of absorbent, the sensitivity is 0.02 ppm. Smaller concentrations could be determined, depending largely on the ability to measure the inked lines on the polarogram. Air samples can be determined with an accuracy of $\pm$ 10 percent and a reproducibility of 3 percent.

According to Kolthoff and Miller [42] only one of the two tautomers of sulfurous acid is reducible at the dropping mercury electrode, and at pH 4, there is less of the reducible than of the nonreducible tautomer present. The fuchsin-formaldehyde colorimetric determination involves a similar situation in that only one of the tautomers results in the formation of a red color. The same conditions of collection efficiency and reagent stability also apply since the scrubbing media used in the methods are identical.

Sulfur compounds generally do not interfere with the polarographic method. Cystine does not interfere with the analysis but reacts with the SO_2 while in

the collecting medium. (The disulfide group is reduced to sulfhydryl by SO_2.) Nitrites are reduced at the dropping mercury electrode at a more negative potential than SO_2 and presumably would interfere only if present in very large concentration.

Iodimetric Methods

IODINE METHOD [43]

SO_2 in the air is removed and concentrated by scrubbing through a 0.1 normal sodium hydroxide solution contained in a midget or standard impinger at a sampling rate of 0.1 and 1 cfm respectively. The solution is subsequently acidified and titrated with a standard 0.001 normal iodine solution. This method of sampling is not particularly suitable for field work unless a mobile laboratory is available that permits titration of the sample within 24 hours after collection. Negligible losses of SO_2 strength result from the storage of the sample solution in the concentration range reported for a 24-hour period. [21]

For a 30-cubic-foot air sample collected at 1 cfm for 30 minutes, a sensitivity of 0.01 ppm is obtained. The reproducibility for the combined analytical procedure is 10 percent in the range 0.10 to 1.3 ppm with the relative standard deviation decreasing with increasing concentrations. [4] It was found that recoveries by the iodimetric method in the range of concentration of 0.10 to 1.3 ppm were lower than by West-Gaeke or hydrogen peroxide methods. Oxidizing materials such as nitrogen dioxide and ozone would result in a decrease in recovery, or amount of SO_2 measured, and the presence of reducing materials such as H_2S in the airstream would result in a positive interference.

DIRECT IODINE METHOD

Pearce and Schrenk [44] described a method in which SO_2 in air is absorbed and oxidized directly in a neutral starch-KI-iodine solution. Air is sampled through a midget impinger at 0.1 cfm. The time required for disappearance of the blue color is noted and the amount of SO_2 present is calculated from the amount of iodine originally present. If sampling time is too long, the results are relatively high owing to loss of iodine by aeration of the absorbing solution. The loss is decreased with increasing amounts of KI. A recovery of better than 83 percent is reported and is independent of concentration. The method is nonspecific and is applicable in the presence of relatively small amounts of other oxidizing or reducing materials. A sensitivity of 0.1 ppm is attained for a 0.5-cubic-foot air sample collected for 5 minutes.

Kitano [45] utilized a second bubbler downstream connected in series and containing standard thiosulfate solution. Exposure to carbon dioxide and oxygen did not affect the strength of the thiosulfate solution. In this manner any iodine lost during aeration would be trapped by the second bubbler and could therefore be accountable. The bubbler containing the iodine-absorbing reagent was maintained at 0°C. All-glass tubing was used to prevent any losses of volatilized or entrained iodine solution. If a hand pump is used, the method is useful for a rapid, direct approximation of SO_2 levels in air since no accessory equipment is required in the analysis.

IODINE-THIOSULFATE METHOD [36,46-48]

SO_2 in air is collected by absorption in a fritted bubbler containing 50 milliliters of 0.005 normal iodine at 5 liters per minute for 10 to 30 minutes. The amount of iodine consumed is proportional to the amount of SO_2 collected and is determined by titration with 0.005 normal thiosulfate solution. It was found that the error due to evaporation of liquid is relatively small as is that due to loss of iodine if 25 percent KI is used. For a 30-minute air sample, a sensitivity of 0.4 ppm is attained. This may be increased by reducing the strength of the iodine and thiosulfate reagents. Griffin and Skinner [48] suggested the use of an air blank obtained by simultaneously sampling through a bubbler preceded by a soda-lime tower to remove all SO_2 at the source.

TURBIDIMETRIC METHOD [49,50]

Matty and Diehl [50] used a phototurbidimetric method developed by Corbett [49] for the measurement of SO_2 in flue gas. SO_2 is removed from the gas stream by absorption in hydrogen peroxide reagent and is subsequently determined as sulfate turbidimetrically in an acid isopropyl alcohol medium. The turbidity is determined 5 minutes after the addition of 1 milliliter of 1 percent $BaCl_2$ solution. Since optical density changes with time owing to the degree of completeness of precipitation and changes in crystal size, the time elapsed between the addition of precipitant and photoelectric measurement is critical and should be standardized. The range of concentration determinable is 0.1 to 0.4 milligram of SO_4 per 25 milliliters when photometric measurement is made with a light path of 25 millimeters. A very close correlation with the gravimetric sulfate procedure was obtained over this range of concentration. A 30-cubic-foot gas or air sample may be determined with a sensitivity of 0.4 ppm by using these calibration data. The sensitivity of the method may be increased by increasing the length of the cell path or by sampling for a longer period of time to obtain a larger sample. The addition of barium chloride in solid rather than in solution form was found to yield a more lasting suspension of barium sulfate. [51] Volmer and Frohlich [52] stabilized the suspension with an acid-glycerine-alchol-gum arabic mixture at a pH of 3.2.

Mathers [40] described a turbidimetric method in which SO_2 is collected in a neutral 1 percent lead acetate solution. The amount of $PbSO_3$ formed is determined turbidimetrically at a wavelength of 600 millimicrons. The sensitivity of the method is 0.1 milligram as SO_3. Materials other than SO_2 that form insoluble compounds with lead ion interfere in the determination although $PbSO_3$ has a lower solubility product than do lead derivatives of other commonly occurring gases and aerosols such as hydrogen sulfide and sulfuric acid.

Cumulative Methods

LEAD PEROXIDE CANDLE METHOD

The lead peroxide (PbO_2) method of measuring the extent of atmospheric pollution by SO_2 was developed in England by the Department of Scientific and Industrial Research (DSIR) in 1932 and has been used extensively there ever since; it has been applied only recently in this country. [53,54]

The object was to provide an index of the activity of SO_2 in the atmosphere as a measure of an aging effect on fabric and buildings and of its effect on the corrosion of metals. The method is based on measuring the sulfation caused by gaseous SO_2 in ambient air by exposing PbO_2 paste. It is a cumulative method similar to the usual measurement of dust fall. The candle used in England consists of a porcelain cylinder about 10 centimeters in circumference. A 10 x 10-centimeter piece of cotton gauze is wrapped around the porcelain form as reinforcement and the active reagent is applied. The active reagent is applied in the form of a paste consisting of 8 grams of PbO_2 in about 5 milliliters of a gum tragacanth solution prepared by dissolving the gum in ethyl alcohol and diluting with distilled water. The candle is exposed in a shelter, which protects the reactive surface from rain, for a period of 1 month; shorter or longer exposure periods may be used depending upon the SO_2 activity of the atmosphere. After exposure, the material is stripped from the candle with sodium carbonate, and the amount of sulfate is determined by the standard gravimetric procedure. The results are reported as milligrams of SO_3 per 100 square centimeters of PbO_2 per day.

Wilsdon and McConnell [55] indicated that the rate of sulfate formation is proportional to SO_2 concentrations in the atmosphere, at least up to 15 percent conversion of the reactive material. From experiments in a wind tunnel, the rate of reaction was found to vary inversely as the 4th root of the wind velocity. An increase in temperature of 1°C increased the reaction rate about

GPO 813-685-4

0.4 percent. The reaction rate also increased considerably when the surface was wet. Conversion to $PbSO_4$ was found to be a function of PbO_2 particle size. The authors noted a change in reaction rate with different batches of PbO_2. In the work done in England, a large batch of PbO_2 sufficient to last for several years was obtained. The results obtained by this method correlated very well with data secured by other methods (volumetric) when the results were corrected for wind velocity and temperature. These experiments were conducted at SO_2 concentrations (30 to 300 ppm) much larger than those in the atmosphere.

Parker and Richards [56] estimated that errors of sampling and analysis are about 10 percent. Eight PbO_2 cylinders were exposed simultaneously for a period of 6 months during 1948-1949. The mean rate of sulfation was 2.6 milligrams of SO_3 per 100 square centimeters per day and the standard deviation of one observation was 7 percent of the mean.

Thomas and Davidson [57] employed PbO_2 cylinders to obtain relative sulfation values at selected sites in the vicinity of large, coal-burning steam plants. No deterioration in the rate of reactivity of PbO_2 with SO_2 was noted in periods of exposure as long as 4 months. A relatively low degree of correlation was obtained for sulfation rates and SO_2 dosage as measured by the Thomas Autometer. This was attributed principally to the typically low average SO_2 dosage at most sites near a single source. At the site of maximum exposure, the average SO_2 concentration was 0.02 ppm. Rather than compare field values with a sealed laboratory control, control cylinders were operated at remote sites 60 to 70 miles distant from a sulfur dioxide source. Sulfation rates varied from 0.02 to 0.04 milligram of SO_3 per 100 square centimeters per day. This value of about 0.03 milligram of SO_3 per 100 square centimeters per day is considered to be a realistic value for clean air, which is an order of magnitude greater than that established from sealed-source laboratory controls. The basic cylinder employed at TVA consists of an ordinary 8-ounce, short-form glass jar. Eight grams of PbO_2 paste are painted on a 100-square-centimeter band of cotton gauze stapled around the glass jar. Freshly coated cylinders are dried overnight in a desiccator and screwed into the smaller of two concentric, bradded and soldered-metal jar tops. This assembly is screwed into a wide-mouthed, 32-ounce glass jar, which serves as a convenient carrier for shipment and storage. At the site of the field station, the inner small jar with PbO_2 coating is inverted and screwed into a jar top permanently mounted on the base of a louvered shelter. The shelter is mounted on a 4-foot post. Supports such as utility poles may be used.

Foran et al. [58] found that measurement of SO_2 activity by means of PbO_2 candles was well suited to measuring relative concentrations of SO_2 in conjunction with metal corrosion studies. Severity of corrosion of zinc and stain-

less steel panels closely correlated with SO_2 dosage as measured by the PbO_2 candle method. Wilkins [59] compared the relative values of SO_2 concentrations determined by the H_2O_2 and the PbO_2 candle methods. A close correlation of sulfation rate with SO_2 concentration was obtained. The conversion factor from ppm to sulfation rate was milligrams per 100 square centimeters per day x 0.04 = SO_2, ppm. It was found that the factor by which the PbO_2 reading must be multiplied to give the concentration of SO_2 varied from month to month at any given site and from site to site for any given month.[8] Yearly means for each of seven sites in and around London were obtained by dividing the concentration of SO_2 in micrograms per cubic meter by the rate of sulfation of PbO_2 in milligrams SO_3 per 100 square centimeters per day by the H_2O_2 method. The yearly means of the sites varied from 63 to 172 with an average value of 112. These results show no simple connection between concentration of SO_2 and PbO_2 readings. The author concluded that PbO_2 readings at any one site should not be used to give an indication of change in concentration from one month to another. Comparisons between one year and another are also not very precise, though they may be useful in defining areas of gross pollution. Nevertheless, if trends over a number of years are considered, for example, by a comparison of one 5-year average with the next or of 5-year running averages, the variation due to wind, weather, etc., tends to become small and the measurement of SO_2 more precise: the 5-year average has long been recommended by the DSIR for this purpose.

In any district of limited size, for example, the area surrounding a particular source such as a power station, it is a reasonable assumption that the cylinders would be exposed to the same weather conditions — *wind, humidity,* temperature— so that the rate of sulfation should bear the same relation to concentrations of SO_2 for each. The pattern of concentration so obtained should, therefore, be valid, even though the absolute value for each month can be obtained only by comparison with data obtained from other SO_2 apparatus.

TEST PAPER METHOD

Buck [60] described a cumulative method for the determination of SO_2. Filter paper is impregnated with a mixture of $KHCO_3$ - H_2O - glycerine and the treated paper is then exposed to ambient air for 100 hours. After exposure the material is stripped from the filter paper, and the amount of sulfate is determined by the standard gravimetric procedure. Further investigation is necessary to determine sulfation values relative to SO_2 concentration.

Pate et al.[61] used membrane filters impregnated with potassium bicarbonate to collect SO_2 in aspirated air samples. A 95 percent collection efficiency was obtained in the concentration range 0.1 to 10 ppm.

Hugen [62] sampled SO_2 in air using Whatman No. 1 filters impregnated with potassium hydroxide and glycerol. A collection efficiency of greater than 95 percent was obtained at relative humidities of greater than 25 percent,

but below 25 percent, collection efficiencies dropped sharply. SO_2 was subsequently analyzed by washing the filter with water, neutralizing with HCl, and applying the West-Gaeke colorimetric method. The stability of the potassium sulfite formed on the filter was poor in the presence of water vapor, but the filter could be stored for 2 weeks without appreciable oxidation if the filters were stored in a dry atmosphere.

Detector Tubes [63]

Gas detector tubes are generally nonspecific and not sufficiently sensitive to measure concentrations of pollutants found in ambient air. The present state of gas-detecting tubes is that they are semiquantitative devices useful for preliminary survey and screening in industrial hygiene work. Test kits are being used more and more in industrial hygiene investigations because they are relatively inexpensive and capable of detecting hazardous concentrations immediately so that corrective measures can be taken. Detector tubes are, however, subject to interferences, and the findings are frequently estimates only, and abuse is, therefore, possible in the hands of untrained personnel. Techniques for the calibration of gas-detecting tubes are described by Kusnetz et al. [64]

INSTRUMENTAL METHODS CONSIDERED IN ADDITION TO RECOMMENDED METHODS

Potentiometric Method [20,65,66]

The apparatus consists of a sampling probe, flow control device, absorption-titration cell, current-generating electrodes, oxidation-reduction-sensing electrode system, amplifier, milliampere recorder, and gas pump. Air is drawn continuously through the titration cell at a fixed rate of approximately 1 liter per minute. The zero level is automatically recorded periodically by passage of the air sample through a charcoal-soda lime filter. SO_2 in the measured air stream is absorbed in an acidified bromide solution contained in the

titration cell. The instrument is initially adjusted to generate continuously a comparatively low level of bromine in the acid-bromide reagent. A pair of electrolyzing electrodes is used in which bromine is generated at one electrode and hydrogen is evolved in the second electrode. Any compound in the air stream that is oxidized by bromine will proportionately reduce the initially selected bromine concentration. This reduction in bromine concentration changes the oxidation reduction potential of the reagent, which is immediately sensed by the appropriate sensor electrode system. This, in turn, electronically calls for generation of sufficient additional bromine to maintain the original bromine concentration. The electric current required to generate this additional bromine is a measure of the reducing gas in the atmosphere.

Oxidizable sulfur compounds other than SO_2 such as H_2S, mercaptans, organic sulfides, and disulfides are recorded by the analyzer. Some gases such as olefins, diolefins, and phenolic compounds would be titrated to a limited degree. The presence of these interferences would yield relatively high results for SO_2. Chlorine, bromine, chlorine dioxide, nitrogen dioxide, or ozone would reduce the bromine demand and would be manifested by comparatively low results for SO_2. It would be possible to conduct a prior separation of an atmospheric mixture of sulfur-containing compounds before passing the sample into the analyzer. [67] An automatic multiple-selector valve operating on a timed sequence could pass the air sample sequentially through various filters and scrubbers as follows:

1. Bismuth subcarbonate-H_2SO_4 solution to remove H_2S;
2. potassium dichromate solution to remove H_2S and SO_2;
3. alkaline $CdSO_4$ solution to remove H_2S, SO_2, and RSH;
4. activated charcoal-soda lime to remove all reactive constituents.

Pyrolysis offers the possibility of converting mixtures of sulfur gases to either H_2S or SO_2. Field and Oldach [68] converted a mixture of sulfur compounds to H_2S by passing a sampled stream of air with hydrogen over alumina at 900°C. Thomas et al. [69] oxidized H_2S, mercaptans, and other sulfur compounds to SO_2 by passing the sampled air through a silica combustion tube containing an electrically heated, spiral, platinum wire.

The range of SO_2 detectable by the instrument is 0.1 to 10 ppm with a sensitivity of 0.1 ppm and a reproducibility of 0.2 ppm. A 90 percent response to a change in concentration is effected in 30 seconds.

Nader and Dolphin [70] have developed a circuit modification that increases instrument sensitivity by a factor of 10. This has, however, resulted in excessive background noise level and zero drift. Development of an accessory circuit to arrange for automatic adjustment of the generating current is currently in process and will permit the unattended, continuous monitoring of atmospheric SO_2 at the increased sensitivity. McKee and Rollwitz [71] pursued a similar modification and increased instrument sensitivity to one scale division

per 0.01 ppm SO_2; full-scale deflection corresponded to 0.75 ppm. A potentiometric recorder was substituted for the recording milliameter. The noise level was reduced to a satisfactory level by an electronic filter. Zero drift was still the greatest difficulty encountered, and occasionally no record was obtained when the zero point drifted off the scale.

The apparatus is calibrated against standard mixtures of inert gas with SO_2. The calibrating mixtures may be prepared in a tank of known capacity pressured to from 100 to 200 psig containing metered volumes of SO_2 gas.[20] SO_2 cylinders prepared in this manner will decrease in strength by 5 to 10 percent in 2 months and should therefore be used within this time. Standard SO_2 mixtures may also be prepared in gas test chambers or in collapsible mylar or teflon bags and then fed into the analyzer at the normal rate of flow. Several calibration points within the full-scale reading of the instrument should be obtained.

Carpenter and Sparkman [72] adapted the analyzer for field mobile sampling in a motor vehicle and in a helicopter. The analyzer has also been operated in a helicopter by Gartrell and Carpenter [73] in the study of dispersion patterns by measuring SO_2 concentration in a plume.

Photometric Methods

ANALYZER "A"

Katz [74,75] described a continuous, automatic analyzer for SO_2 that employs photoelectric cells and a recording potentiometer to indicate the increase in light transmission of blue starch-iodine solutions after aspiration with contaminated air. The instrument has a range of 0.01 to 1 ppm or more, depending upon the volume and concentration of solution in the absorbers and the amount of air sample passed through the solution. This instrument is not commercially available. The gas bubblers consist of pyrex salvarsan tubes of 350-milliliter capacity. The instrument operates on a 2-minute time cycle, the solution in one absorber being aspirated at a measured flow rate for this interval after which the air is passed through the second absorber, by the opening and closing of appropriate, cam-operated, poppet valves. The aspiration is continued alternately for eight successive operations in each absorber. At the end of this period of about 32 minutes, the solution in each absorber is drained successively, and fresh solution is delivered from a stock bottle of 20-liter capacity. The light transmission through the blue starch-iodine

solution is recorded during the 2-minute quiescent period following each aspiration cycle by means of a recording potentiometer with a scale range of 0 to 50 millivolts. The change in concentration of the blue starch-iodine solution is determined by using two photronic cells to measure the light transmission through each absorber from a constant source supplied by a 20-watt lamp. The light source is mounted midway between the absorbers, and the photo cells are mounted behind each one. Output current from the cells is passed through a standard resistance box, and the voltage drop across the 0-to-500-ohm terminals is measured by means of the recording potentiometer.

The recorder is calibrated by determining the potentiometer reading for a series of starch-iodine solutions varying in normality from 8×10^{-5} to 2×10^{-5} during the operation of the analyzer with SO_2 -free air. Reproducible results are obtained on iodine solutions of equivalent normality. Experiments indicate that the starch-iodine solution used remains stable after aspiration with SO_2 -free air at rates of about 10 liters per minute for periods of 30 minutes. Only a high grade of starch, which gives the characteristic blue color with dilute iodine solution, is suitable for this work. Grades that yield a purple tinge are unsatisfactory. The stock solutions are stable for 1 week when stored in a dark, cool room provided the vessels are maintained in a clean, sterile condition.

Sulfur trioxide, sulfuric acid mist or sulfate, and unsaturated hydrocarbons do not interfere in this method. Oxidizing and reducing materials such as H_2S and NO_2 do, however, interfere, and the method is not applicable in atmospheres where these materials are likely to be present in appreciable quantities.

ANALYZER "B"

Adams, Dana, and Koppe [76] developed a versatile, continuous, automatic, photometric analyzer based on the dosimeter sampling principle. A small volume of reagent sensitive to a particular ion or class of compounds is circulated continuously in the air-reagent contactor system until a preselected concentration of the pollutant under study is accumulated. When this has been reached, the instrument automatically discharges the spent reagent and injects a measured volume of fresh reagent. Sampling is then continued until another cycle is completed by the accumulation of the standard quantity of pollutant. The pollutant concentrations may be recorded as either a tape record of the time necessary to accumulate each equivalent quantity of the pollutant under study or as a continuously integrated recorder chart of the rate of accumulation of the pollutant during each dosimeter period. This instrument is suitable for the automatic recording of any pollutant for which a suitable colorimetric reagent can be developed.

A starch-iodine reagent is used for the photometric determination of atmospheric SO_2. It was found that the partially bleached blue color was more unstable under conditions of continuous aeration than was the unbleached blue

color. A reasonably stable reagent that may be aerated at approximately 0.1 cfm for periods of more than 12 hours was produced by the addition of small quantities of N-acetyl-p-aminophenol and mannitol. It was also found that the blue color of the reagent was extremely sensitive to temperature. Furthermore, the color was found to deteriorate rapidly when stored in the dark at elevated temperatures of 120°F. To minimize these effects, the dosimeter cabinet was thermostatted at 75°F with a refrigerative compressor to maintain this temperature. Light absorbance measurements are conducted with a 50-watt projection lamp and an optical filter peaking at 575 millimicrons.

The prepared reagent is stored in a black reagent bottle in the automatic analyzer. A drop of mercury is kept in the storage bottle to act as a fungicide. The reagent has been found to remain stable up to 1 week when handled in this manner. A soda lime-activated charcoal trap on the reagent bottle's air inlet protects the reagent from possible contamination by air pollutants.

A countercurrent type of air-reagent contacting system is employed in which a small batch of reagent is continuously circulated through an optical flow cell. Small evaporation losses are continuously sensed and dropwise additions of distilled water are automatically made to maintain the original volume. The sampled air is drawn through a rotameter, and the air volume is regulated by means of a built-in air bypass on the vacuum side of the air pump. Air entering under suction lifts the reagent, which has fallen by gravity through the optical path, up through the contacting column. The scrubbed air is exhausted through a tube at the top of the system to the vacuum pump, and the reagent is maintained within the optical cell by means of the capillary tip at the lower end of the cell. The cycling of the reagent with the stream of continuously sampled air continues until:

(1) A pre-selected concentration of the pollutant is accumulated, or
(2) a maximum time over which the reagent remains stable is exceeded, or
(3) the reset button is manually operated.

Further investigation should be conducted to establish the practicality of the system under field conditions for the measurement of SO_2. Instrument performance data have been supplied by the manufacturer for the measurement of atmospheric fluorides but no such specifications have been made available as yet for SO_2 analysis.

ANALYZER "C"

The Portable SO_2 Meter was developed in the Central Electricity Research Laboratory by Cummings and Redfearn. [77] SO_2 in air reacts with a starch-iodine reagent in a countercurrent absorption column. The amounts of light absorbed by the unchanged and the partially decolorized reagent are compared by photoelectric cells connected to a galvanometer. It was found that the reagent as recommended by Katz [74] was stable for several days when kept in stoppered polyethylene bottles. The light absorption of batches of

reagent made over a period of 1 year varied by less than 1 percent. With the countercurrent absorption column and the rates of air and reagent flow used for this instrument, no iodine was volatilized from the solution by the incoming air.

The starch-iodine reagent contained in a 1-liter aspirator bottle, which is fitted with a constant-head device, flows by gravity through a control valve into the bottom of a liquid cell. From here, the reagent passes through a rotameter, which indicates the flow rate to the top of the absorption column where it flows down the spiral path. To avoid corrosion by the starch-iodine reagent, a korannite float and tantalum spring float stops are used.

Air is drawn by means of a DC blower into the bottom of the absorption column where the SO_2 reacts with the reagent. If a check on the zero is required, air is first drawn through soda-lime by means of stopcocks. Air leaves the top of the absorber via a rotameter and blower. The partially decolorized reagent flows from the bottom of the absorber into the bottom of the glass liquid cell and then runs to a waste bottle.

Comparison of the absorbance of the reacted to unreacted reagent is made in a photocell compartment consisting of a single light source (6 volts, 0.2 amp), condensers to form parallel beams of light, red filters, and two photocells mounted behind the glass cells. The unbalanced output of the photocells is measured by a galvanometer. The meter is sensitive to 0.01 ppm in the range 0 to 0.50 ppm. This range may be extended by reducing the flow of air to the instrument; the sensitivity decreases in proportion to the increase in range. The readings obtained must be regarded as 2-minute running averages because there is a time lag of about 2 minutes before a steady reading is obtained for a particular SO_2 concentration.

If the instrument is operated in a motor vehicle, power can be drawn from the 12-volt battery. For use away from roads a 12-volt battery can be incorporated within the instrument case.

This instrument was designed for rapid measurement at various points in a selected area; thus, there is always an operator with the instrument, and a recorder is unnecessary. Since the total output of the photocell is about 0.25 millivolt, it would not be practical to feed the output to a normal recorder.

ANALYZER "D"

Helwig and Gordon [78] converted an automatic, conductimetric, SO_2 analyzer to an automatic, continuous-recording, colorimetric analyzer by replacing the conductivity cells with colorimeter cells having a 2-centimeter path and a mercury lamp light source. A synchroverter was added and necessary circuit changes were made to use a 0- to 10-millivolt recorder. This instrument is not commercially available.

The pararosaniline-formaldehyde reagent developed by West and Gaeke [1] was selected as the chromophoric reagent for use in the automatic recorder. It was found that the rate and magnitude of the color response to SO_2 were greater in the absence of sodium tetrachloromercurate. Further increase in sensitivity was obtained by decreasing the dye concentration to one half of that suggested by the authors. The mixed reagent was stable for 2 weeks.

Collection efficiency of the countercurrent absorption column varied with airflow rate. At an airflow rate of 0.25 liter per minute, the collection efficiency was found to be 95 to 97 percent. Efficiency dropped to 73 to 75 percent at a flow rate of 1 liter per minute. A system was established to detect SO_2 in the concentration range 0 to 5 ppm. By varying reagent and sample flow, the scale can be reduced or expanded.

Static calibration of the instrument was conducted with standard solutions of sodium meta bisulfite equivalent to 1 to 5 ppm of SO_2 on the basis of an airflow of 0.25 liter per minute and a reagent flow of 3.3 milliliters per minute.

An instrument sensitivity of 0.02 ppm and excellent reproducibility were reported in the 1-to-5-ppm range of concentration. NO_2 and O_3 in concentrations of less than 1 ppm produced negligible interference on SO_2 measurement.

Air Ionization Method [79]

The aerosol ionization detector consists essentially of an ionization chamber with a stainless steel cylinder serving as an outer electrode and a heavy wire as the inner electrode. Fifty to 100 micrograms of radium is placed along the surface of the cylinder to serve as an alpha source. The two electrodes are under a voltage potential difference that causes a flow of ion current between them. The presence of small concentrations of particulate matter causes a marked drop in the flow of ion current.

A compensated detection system is used in the analyzer. The sample stream is divided between two similar ion chambers. The difference in ion current produced by the unreacted and reacted sample stream is detected by an electrometer measuring circuit and is fed into a suitable recorder.

To use this principle for the determination of gases and vapors, it is necessary to form small particles from the material being analyzed. Three methods may be used to accomplish this: (1) Reaction of the material with a reagent to produce particulate matter, (2) pyrolysis or irradiation with ultraviolet light, or (3) a combination of both.

The instrument is sensitized to SO_2 by pyrolysis in the presence of CuO. A gas-solid reaction occurs and copper sulfate is formed.

An instrument range of 0 to 10 ppm SO_2 is obtained with this sensitization method. The method is nonspecific since any material capable of salt formation with CuO at elevated temperatures will interfere. Additional investigation is required concerning instrument performance under conditions of continuous air monitoring, reproducibility, sensitivity, and the relative effects of interfering materials.

REFERENCES

1. West, P. W., Gaeke, G. C., Fixation of Sulfur Dioxide as Disulfitomercurate (II), Subsequent Colorimetric Estimation, Anal. Chem., 28:1916. 1956.

2. Nauman, R. V., West, F. W., Tron, F., Gaeke, G. C., Spectrophotometric Study of the Schiff Reaction as Applied to the Quantitative Determination of Sulfur Dioxide, Anal. Chem., 32:1307. 1960.

3. McCaldin, R. O., Hendrickson, E. R., Use of a Gas Chamber for Testing Air Samplers, J. Am. Ind. Hyg. Assoc., 20:509. 1959.

4. Terraglio, F. P., Manganelli, R. M., Laboratory Evaluation of SO_2 Methods, Anal. Chem., 34:675. 1962.

5. Perry, W. H., Tabor, E. C., National Air Sampling Network Measurement of SO_2 and NO_2, Arch. Environmental Health, 4:44. 1962.

6. West, P. W., Ordoveza, F., Elimination of Nitrogen Dioxide Interference in the Determination of Sulfur Dioxide, Anal. Chem., 34:1324. 1962.

7. Zurlo, N., Griffini, A. M., Measurement of Sulfur Dioxide Content of the Air in the Presence of Nitrogen and Heavy Metals, Med. d. Lavoro, 5:330. 1962.

8. Craxford, S. R., Slimming, D. W., Wilkins, E. T., The Measurement of Atmospheric Pollution: The Accuracy of the Instruments and the Significance of the Results, Proceeding of the Harrogate Conference. London, England. 1960.

9. Pate, J. B., Lodge, J. P., Wartburg, A. F., Effect of Pararosaniline in the Trace Determination of Sulfur Dioxide, Anal. Chem., 34:1660. 1962.

10. Jacobs, M. B., The Chemical Analysis of Air Pollutants, Interscience, New York. 1960.

11. Jacobs, M. B., Greenburg, L., Sulphur Dioxide in New York City Atmosphere, Ind. Eng. Chem., 48:1517. 1956.

12. Perley, G. A., Langsdorf, B. T., Problems in the Recording of Sulfur Dioxide in Polluted Atmospheres, Chap. 69, Proceedings of the United States Technical Conference in Air Pollution, L. C. McCabe, ed., McGraw-Hill, New York. 1952.

13. Yocum, J. E., Richardson, R. L., Saslaw, X. M., Chapman, S., The Effect of Hydrogen Chloride on the Operation of the Thomas Autometer, Proceedings 49th Annual Meeting of the Air Pollution Control Association, Buffalo, N. Y. 1956.

14. Jacobs, M. B., Braverman, M. M., Hochheiser, S., Ultrasensitive Conductometric Measurement of Sulfur Dioxide in Air, Instrument Society of America Meeting, Paper No. 56-32-3, Sept. 1956.

15. Reece, G. M., White, B., Drinker, P., Determination and Recording of Carbon Disulfide and Hydrogen Sulfide in the Viscose-Rayon Industry, J. Ind. Hyg. Tox., 22:416. 1940.

16. Thomas, M. D., Ivie, J. O., Abersold, N. N., Hendricks, R. H., Automatic Apparatus for Determination of Small Concentrations of Sulphur Dioxide in Air Application to Hydrogen Sulfide, Mercaptans, and Other Sulfur and Chlorine Compounds, Ind. Eng. Chem. Anal. Ed., 15:287. 1943.

17. Cummings, W. G., Redfearn, M. W., Instruments for Measuring Small Quantities of Sulfur Dioxide in the Atmosphere, J. Inst. of Fuel, 30:628. 1957.

18. Air Sampling Instruments, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio. 1962.

19. Recommended Methods in Air Pollution Measurements, California State Department of Public Health, Berkeley, Calif. 1960.

20. ASTM Standards on Methods of Atmospheric Sampling and Analysis, American Society for Testing Materials, Philadelphia, Pa. 2nd Ed., 1962.

21. Hochheiser, S., Braverman, M. M., Jacobs, M. B., Comparison of Methods for the Determination of Atmospheric Sulphur Dioxide, presented at Metropolitan L. I. Subsection, New York Section, ACS Meeting in miniature, Feb. 1955.

22. Paper EPA/AR/4283, Routine Methods for Estimating Sulphur Dioxide in the Air, Organization for European Economic Cooperation, European Productivity Agency, Paris, France. 1961.

23. Welch, A. F., Terry, J. P., Development in the Measurement of Atmospheric Sulfur Dioxide, J. Am. Ind. Hyg. Assoc., 21:316. 1960.

24. Paulus, H. J., Floyd, E. P., Byers, P. H., Determination of Sulphur Dioxide in Atmospheric Samples. Comparison of a Colorimetric and a Polarographic Method, J. Am. Ind. Hyg. Assoc. Quarterly, 15:4. 1954.

25. Urone, P. F., Boggs, W. E., Acid-Bleached Fuchsin in Determination of Sulfur Dioxide in the Atmosphere, Anal. Chem., 23:1517. 1951.

26. Steigmann, A., A New Color Reaction for Sulfurous Acid, The Thiol Group and Formaldehyde, Anal. Chem., 22:493. 1950.

27. Grant, W. N., Colorimetric Determination of Sulphur Dioxide, Ind. Eng. Chem. Anal. Ed., 19:245. 1947.

28. Stang, A. M., Zatek, J. E., Robson, C. D., A Colorimetric Method for the Determination of Sulfur Dioxide in Air, Am. Ind. Hyg. Assoc. Quarterly, 12:5. 1951.

29. Moore, G. E., Cole, A. F. W., Katz, M., The Concurrent Determination of Sulphur Dioxide and Nitrogen Dioxide in the Atmosphere, J. Air Poll. Control Assoc., 7:25. 1957.

30. Determination of Sulphur Dioxide in Air, Fuchsin-Formaldehyde Method, American Conference of Governmental Industrial Hygienists, Methods Manual, Cincinnati, Ohio. 1958.

31. Stratman, H., Microanalytical Methods for the Determination of Sulphur Dioxide, Mikrochimica Acta, 6:668. 1954.

32. Kanno, S., The Colorimetric Determination of Sulfur Oxides in the Atmosphere, Intern. J. Air Poll., 1:231. 1959.

33. Bertolocini, R. J., Barney, J. E., Colorimetric Determination of Sulfate Using Barium Chloranilate, Anal. Chem., 29:281. 1957.

34. Hands, G. C., Bartlett, A. F., A Field Method for the Determination of Sulphur Dioxide in Air, Analyst, 85:147. 1960.

35. Dept. of Sci. and Ind. Research. DSIR Methods for the Detection of Toxic Gases in Industry, Leaflet No. 3, H. M. Stationery Office, London, England. 1939.

36. Liddell, E. F., A Reagent for Sulphur Dioxide, Analyst, 80:901. 1955.

37. Klein, B., Microdetermination of Sulfate. A Colorimetric Estimation of the Benzidine Sulfate Precipitate, Ind. Eng. Chem. Anal. Ed., 16:536. 1944.

38. Lambert, J. L., Yaida, S. K., Grother, M. P., Colorimetric Determination of Sulfate Ion, Anal. Chem., 27:800. 1955.

39. Blinn, R. C., Gunther, F. H., Indirect Ultra-Violet Spectrophotometric Determination of Sulphur Dioxide by Means of Plumbous Ion, Analyst, 86:675. 1961.

40. Mathers, A. P., Rapid Determination of Sulphur Dioxide in Wines, J. Assoc. of Agric. Chem., 32:745. 1941.

41. Stephen, B. G., Lindstrom, F., Spectrophotometric Determination of Sulfur Dioxide Suitable for Atmospheric Analysis, Anal. Chem., 36:1308. 1964.

42. Kolthoff, I. M., Miller, C. S., The Reduction of Sulfurous Acid at the Dropping Mercury Electrode, J. Am. Chem. Soc., 63:2818. 1941.

43. Smith, R. B., Fries, B. S. T., Portable Motor-driven Impinger Unit for Determination of Sulfur Dioxide, J. Ind. Hyg., 13:338. 1931.

44. Pearce, S. J., Schrenk, H. H., Determination of Sulfur Dioxide in Air by Means of the Midget Impinger, Bureau of Mines RI 4282. 1948.

45. Kitano, Y., Takakuwa, H., Determination of Hydrogen Sulfide and Sulfur Dioxide in Air, Errors in Iodometry, Japan Analyst, 3:7. 1954.

46. Jacobs, M. B., The Analytical Chemistry of Industrial Poisons, Hazards and Solvents, Interscience, New York. 1959.

47. Elkins, H. B., The Chemistry of Industrial Toxicology, Wiley, New York. 1959.

48. Griffin, S. W., Skinner, W. W., Small Amounts of Sulfur Dioxide in the Atmosphere. Improved Methods for the Determination of Sulphur Dioxide when Present in Low Concentrations in Air, Ind. Eng. Chem., 24:862. 1932.

49. Corbett, P. F., A Phototurbidimetric Method for the Estimation of Sulfur Trioxide in the Presence of Sulfur Dioxide, J. Soc. of Chem. Ind., 67:227. 1948.

50. Matty, R. E., Diehl, E. K., Measuring Flue Gas Sulfur Dioxide and Sulfur Trioxide, Power, 101:94. 1957.

51. Treon, J. F., Crutchfield, W. E., Rapid Turbidimetric Method for the Determination of Sulfates, Ind. Eng. Chem. Anal. Ed., 14:119. 1942.

52. Volmer, W., Frohlich, F. Z., Turbidimetric Determination of Sulfate, Anal. Chem., 126:414, 1944.

53. Department of Scientific and Industrial Research, The Investigation of Atmospheric Pollution, 18th Report, 1931-1932, H. M. Stationery Office, London, England.

54. Ibid, 20th Report, 1933-1934.

55. Wilsdon, B. H., McConnell, F. J., The Measurement of Atmospheric Sulfur Pollution by Means of Lead Peroxide, J. Soc. Chem., Ind., 53:385. 1934.

56. Parker, A., Richards, S. H., Instruments Used for the Measurement of Atmospheric Pollution in Great Britain, Chap. 67; Proceeding of the United States Technical Conference in Air Pollution, L. C. McCabe, ed., McGraw-Hill. 1952.

57. Thomas, F. W., Davidson, C. M., Monitoring Sulfur Dioxide with Lead Peroxide Cylinders, J. Air Poll. Control Assoc., 11:24. 1961.

58. Foran, M. R., Gibbons, E. V., Wellington, J. R., The Measurement of Atmospheric Sulfur Dioxide and Chlorides, Chemistry in Canada, 10:33. 1958.

59. Wilkins, E. T., Air Pollution in London Smog, Mech. Eng., 76:426. 1954.

60. Buck, V. M., Methods for the Determination of Hydrogen Fluoride and Sulfur Dioxide in the Atmosphere, Staub, 21:227. 1961.

61. Pate, J. B., et al., The Use of Impregnated Filters to Collect Traces of Gases in the Atmosphere, Anal. Chem. Acta., 28:341. 1963.

62. Hugen, C., The Sampling of Sulfur Dioxide in Air with Impregnated Filters, Anal. Chem. Acta, 28:349. 1963.

63. Gisclard, J., The Use of Detectors and Test Kits in Industrial Hygiene Investigations, AMA Arch. Ind. Health, 21:250. 1960.

64. Kusnetz, H. L., Saltzman, B. E., Lanier, M. E., Calibration and Evaluation of Gas Detecting Tubes, Amer. Ind. Hyg. Assoc. J., 21:361. 1960.

65. Dickinson, J. E., The Operation and the Use of Titrilog and the Autometer, Proceedings 49th Annual Meeting of Air Poll. Control Assoc. 1956.

66. Giever, P. M., Cook, W. A., Automatic Recording Instruments As Applied to Air Analysis, Arch. of Ind. Health and Occ. Med., 21:233. 1960.

67. Washburn, H. W., Austin, R. R., The Continuous Measurement of Sulfur Dioxide and Hydrogen Sulfide Concentrations by Automatic Titration, Chap. 72, Proceedings of the United States Technical Conference in Air Pollution, L. C. McCabe, ed., McGraw-Hill. 1952.

68. Field, E., Oldach, C. S., Conversion of Organic Sulfur to Hydrogen Sulfide for Analysis, Ind. Eng. Chem. Anal. Ed., 18:668. 1946.

69. Thomas, M. D., Ivie, J. O., Abersold, N. N., Hendricks, R. H., Automatic Apparatus for Determination of Small Concentrations of Sulfur Dioxide in Air. Application to Hydrogen Sulfide, Mercaptans and Other Sulfur and Chlorine Compounds, Ind. Eng. Chem. Anal. Ed., 15:287. 1943.

70. Nader, J. S., Dolphin, J. L., Improved Titrilog Sensitivity, J. Air Poll. Control Assoc., 8:336. 1959.

71. McKee, H. C., Rolwitz, W. L., Improved Titrilog Sensitivity, Field Performance and Evaluation, J. Air Poll. Control Assoc., 8:338. 1959.

72. Carpenter, S. B., Sparkman, R. E., Adaptation of Titrilog for Field Mobile Sampling, J. Air Poll. Control Assoc., 5:195. 1956.

73. Gartrell, F. E., Carpenter, S. B., Aerial Sampling by Helicopter, A Method for the Study of Diffusion Patterns, J. Amer. Meteorol. Soc., 12:215. 1955.

74. Katz, M., The Photoelectric Determination of Atmospheric Sulphur Dioxide by Dilute Starch-Iodine Solutions, Chap. 71, Proceedings of the United States Technical Conference in Air Pollution, L. C. McCabe, Ed., McGraw-Hill, New York. 1952.

75. Katz, M., Photoelectric Determination of Atmospheric Sulfur Dioxide Employing Dilute Starch-Iodine Solution, Anal. Chem., 22:1040. 1950.

76. Adams, D. F., Dana, H. J., Koppe, R.K., Universal Air Pollutant Analyzer, USPHS Contract No. 66512. Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio. 1957.

77. Cummings, W. G., Redfearn, M. W., Instruments for Measuring Small Quantities of Sulfur Dioxide in the Atmosphere, J. Inst. of Fuel, 30:628. 1957.

78. Helwig, H. H., Gordon, C. L., Colorimetric Methods for Continuous Recording Analysis of Atmospheric Sulphur Dioxide, Anal. Chem., 34:1660. 1962.

79. Strange, J. P., Ball, K. E., Barnes, D. O., Continuous Parts Per Billion Recorder for Air Contaminants, Proceedings of the Air Poll. Control Assoc., Cincinnati, Ohio. May 22-26. 1960.

GPO 813-685-5